

## SELECTIVE SORBENTS FOR PURIFICATION OF HYDROCARBONS

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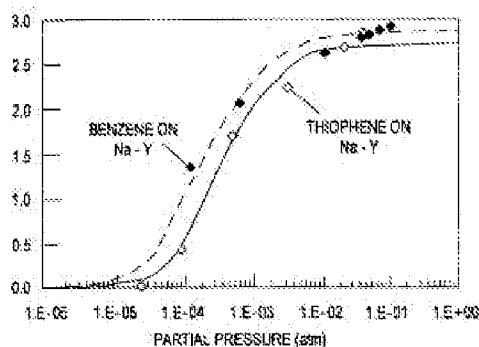
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### Abstract of WO 03020850 (A2)

Cu Y and Ag Y zeolites as selective sorbents for desulfurization of liquid fuels. Thiophene and benzene were used as the model system, and vapor phase isotherms were measured. Compared with NaY, CuY and AgY adsorbed significantly larger amounts of both thiophene and benzene at low pressures. It is hypothesized that this is due to pi-complexation with Cu<sup>+</sup> and Ag<sup>+</sup>. On a per-cation basis, more thiophene was adsorbed by Cu<sup>+</sup> than by Ag<sup>+</sup>, eg. 0.92 molecule/Cu<sup>+</sup> versus 0.42 molecule/Ag<sup>+</sup> at 2x10<sup>-5</sup> atm and 120 DEG C. Molecular orbital calculations confirmed the relative strengths of pi-complexation: thiophene>benzene and Cu<sup>+</sup>>Ag<sup>+</sup>. The experimental heats of adsorption for pi-complexation are in qualitative agreement with theoretical predictions. The invention further comprises a process and sorbents for removal of aromatics from hydrocarbons.



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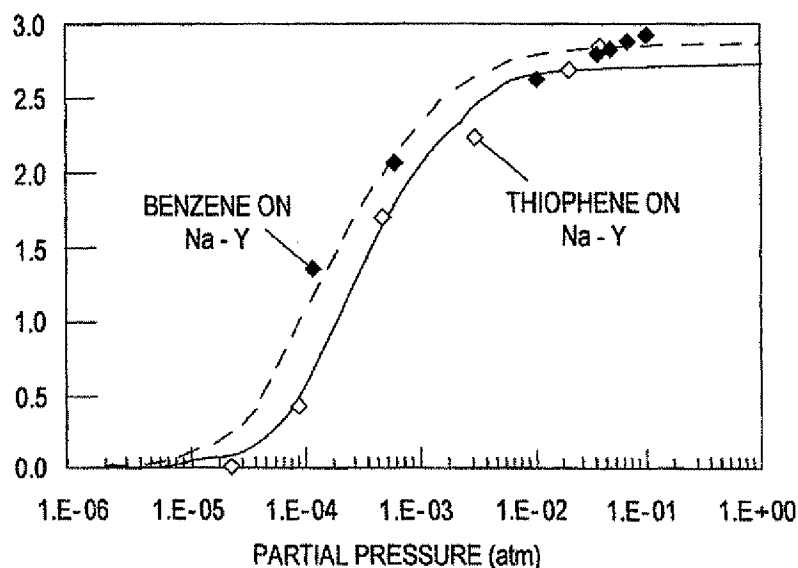
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(54) Title: SELECTIVE SORBENTS FOR PURIFICATION OF HYDROCARBONS



(57) Abstract: Cu Y and Ag Y zeolites as selective sorbents for desulfurization of liquid fuels. Thiophene and benzene were used as the model system, and vapor phase isotherms were measured. Compared with NaY, CuY and AgY adsorbed significantly larger amounts of both thiophene and benzene at low pressures. It is hypothesized that this is due to  $\pi$ -complexation with  $\text{Cu}^+$  and  $\text{Ag}^+$ . On a per-cation basis, more thiophene was adsorbed by  $\text{Cu}^+$  than by  $\text{Ag}^+$ , eg. 0.92 molecule/ $\text{Cu}^+$  versus 0.42 molecule/ $\text{Ag}^+$  at  $2 \times 10^{-5}$  atm and 120 °C. Molecular orbital calculations confirmed the relative strengths of  $\pi$ -complexation: thiophene>benzene and  $\text{Cu}^+$ > $\text{Ag}^+$ . The experimental heats of adsorption for  $\pi$ -complexation are in qualitative agreement with theoretical predictions. The invention further comprises a process and sorbents for removal of aromatics from hydrocarbons.

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PATENT

**SELECTIVE SORBENTS FOR PURIFICATION OF HYDROCARBONS**

**CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Provisional Patent application Serial No. 60/317,158, filed September 4, 2001.

**STATEMENT REGARDING FEDERALLY SPONSORED  
RESEARCH OR DEVELOPMENT**

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**BACKGROUND OF THE INVENTION**

The present invention relates generally to processes for purification of hydrocarbons, and more particularly to adsorption processes using sorbents selective to sulfur compounds and to aromatic compounds.

Petroleum is an extremely complex mixture and consists predominantly of hydrocarbons, as well as compounds containing nitrogen, oxygen, and sulfur. Most petroleums also contain minor amounts of nickel and vanadium. The chemical and physical properties of petroleum vary considerably because of the variations in composition.

The ultimate analysis (elemental composition) of petroleum tends to vary over relatively narrow limits -- carbon: 83.0 to 87.0 percent; hydrogen: 10.0 to 14.0 percent; nitrogen: 0.1 to 1.5 percent; oxygen: 0.1 to 1.5 percent; sulfur: 0.1 to 5.0 percent; metals (nickel plus vanadium): 10 to 500 ppm.

Crude oils are seldom used as fuel because they are more valuable when refined to petroleum products. Distillation separates the crude oil into fractions equivalent in boiling range to gasoline, kerosine, gas oil, lubricating oil, and residual. Thermal or catalytic cracking is used to convert kerosine, gas oil, or residual to gasoline, lower-boiling fractions, and a residual coke. Petrochemical intermediates such as ethylene and propylene are primarily produced by the thermal cracking of light hydrocarbon feedstocks in the presence of steam. Catalytic reforming, isomerization, alkylation, polymerization, hydrogenation, and combinations of these catalytic processes

are used to upgrade the various refinery intermediates into improved gasoline stocks or distillates. The major finished products are usually blends of a number of stocks, plus additives.

Gasoline is a complex mixture of hydrocarbons that distills within the range 100 to 400°F. Commercial gasolines are blends of straight-run, cracked, reformed, and natural gasolines. Straight-run gasoline is recovered from crude petroleum by distillation and contains a large proportion of normal hydrocarbons of the paraffin series. Cracked gasoline is manufactured by heating crude-petroleum distillation fractions or residues under pressure, or by heating with or without pressure in the presence of a catalyst. Heavier hydrocarbons are broken into smaller molecules, some of which distill in the gasoline range. Reformed gasoline is made by passing gasoline fractions over catalysts in such a manner that low-octane-number hydrocarbons are molecularly rearranged to high-octane-number components. Many of the catalysts use platinum and other metals deposited on a silica and/or alumina support. Natural gasoline is obtained from natural gas by liquefying those constituents which boil in the gasoline range either by compression and cooling or by absorption in oil.

Removal of the sulfur-containing compounds is an important operation in petroleum refining, and is achieved by catalytic processes at elevated temperatures and pressures. See, Farrauto, R. J.; Bartholomew, C. H. *Fundamentals of Industrial Catalytic Processes*, Chapman and Hall, New York, 1997. The hydrodesulfurization (HDS) process is efficient in removing thiols and sulfides, but much less effective for heterocyclic diunsaturated sulfur compounds, such as thiophenes and thiophene compounds/derivatives (eg. benzothiophene and dibenzothiophene).

New legislation will require substantial reductions in the sulfur content of transportation fuels. For example, the new U.S. Environmental Protection Agency (EPA) sulfur standards require that the sulfur content in gasoline and diesel fuels for on-board transportation will be 30 ppm and 15 ppm, respectively, drastically decreased from the current acceptable levels of several hundred ppm. Faced with the severely high costs of compliance, a surprising number of refiners are seriously considering reducing or eliminating production of on-board fuels. See Parkinson, G., "Diesel Desulfurization Puts Refiners in a Quandary," *Chemical Engineering*, 2001, February issue, 37.

During the last decade, there have been several published accounts on using adsorption for liquid fuel desulfurization. Commercially available sorbents (i.e., zeolites, activated carbon and activated alumina) were used in all of these studies. Weitkamp et al. reported that thiophene adsorbed more selectively than benzene on ZSM-5 zeolite. See Weitkamp, J.; Schwark, M.; Ernest, S. "Removal of Thiophene Impurities

from Benzene by Selective Adsorption in Zeolite ZSM-5," *J. Chem. Soc. Chem. Commun.*, 1991, 1133. Without being bound to any theory, it is believed that this is because thiophene ( $C_4H_4S$ , also known as thiofuran) has a higher dipole moment (0.55 debye) than benzene (non-polar), although their polarizabilities are similar. Based on this study, King et al. studied selective adsorption of thiophene, methyl- and dimethyl-thiophenes (all with one ring) over toluene and p-xylene, also using ZSM-5. See King, D. L.; Faz, C.; Flynn, T. "Desulfurization of Gasoline Feedstocks for Application in Fuel Reforming," *SAE Paper 2000-01-0002*, Soc. Automotive Engineers, Detroit, 2000. They showed that thiophene was more selectively adsorbed, both based on fixed bed breakthrough experiments. However, the capacities for thiophene were unfortunately quite low (only 1-2% wt. adsorbed at 1% thiophene concentration). Both vapor phase and liquid phase breakthrough experiments were done in these studies, and the results from two phases were consistent.

The pore dimensions of ZSM-5 are 5.2-5.6 Å. Hence, organic sulfur compounds with more than one ring will be sterically hindered or excluded. Zeolites with larger pores, as well as larger pore volumes, would appear to be more desirable than ZSM-5 as the selective sorbents. Indeed, results of Salem and Hamid indicated that 13X zeolite as well as activated carbon had much higher sorption capacities for sulfur compounds. See Salem, A. S. H.; Hamid, H. S. "Removal of Sulfur Compounds from Naphtha Solutions Using Solid Adsorbents," *Chem. Eng. Tech.*, 1997, 20, 342. Based on the data of Salem and Hamid, *Id.*, the capacity for sulfur compounds by 13X zeolite was approximately an order of magnitude higher than that of ZSM-5, when compared with the data of King et al. (cited above) extrapolated to the same conditions.

Activated alumina (Alcoa Selexsorb) has been used in an adsorption process by Irvine. See, for example, U. S. Patent No. 5,730,860 issued to R.L. Irvine in 1998, entitled "Process for Desulfurizing Gasoline and Hydrocarbon Feedstocks."

No direct comparison has been made among these commercial sorbents. Their experiments were mostly done in fixed bed adsorbers, by measuring the breakthrough capacities. Based on the literature, the large pore zeolites (NaX or NaY) are about the same as activated carbon and alumina, in terms of adsorption of thiophene.

Essentially all industrial adsorption processes are based on van der Waals interactions between the sorbate and the sorbent. Chemical bonds have yet to be exploited.

Thus, it would be desirable to provide an adsorption process for selectively removing sulfur compounds from liquid fuels at ambient temperature and pressure, thereby advantageously leading to a major advance in petroleum refining. It

would further be desirable to provide highly selective sorbents for this process, thereby overcoming the drawbacks of current commercial sorbents, which are not desirable for this application.

### SUMMARY OF THE INVENTION

The present invention addresses and solves the above-mentioned drawbacks, and substantially meets the desiderata and advantages enumerated above, by providing a process for removing thiophene and thiophene compounds from liquid fuel. The method comprises the step of contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and a thiophene/thiophene compound-rich adsorbed component. The adsorbent comprises any ion-exchanged zeolite, but in a preferred embodiment, the zeolite is selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof. The zeolite has exchangeable cationic sites, and at least some of the sites have d-block transition metal cation present. The preferential adsorption occurs by  $\pi$ -complexation.

In a further embodiment, the invention comprises a process for removing thiophene and thiophene compounds from liquid fuel. The method comprises the step of contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and a thiophene/thiophene compound-rich adsorbed component. The adsorbent comprises a carrier having a surface area, the carrier having a d-block transition metal compound dispersed on at least some of the surface area. The metal compound releasably retains the thiophenes. The carrier comprises a plurality of pores having a pore size greater than the effective molecular diameter of the thiophene/thiophene compounds. The method may further comprise the step of changing at least one of the pressure and temperature to thereby release the thiophene/thiophene compound-rich component from the adsorbent.

In a further embodiment, the invention comprises a process for selective removal of aromatics from hydrocarbons.

### BRIEF DESCRIPTION OF THE DRAWINGS

Objects, features and advantages of the present invention will become apparent by reference to the following detailed description and drawings, in which:

Fig. 1 is a graph depicting equilibrium isotherms of benzene and thiophene on NaY (Si/Al = 2.43) at 120°C; with the lines being fittings by Langmuir-Freundlich isotherm equation;

Fig. 2 is a graph depicting equilibrium isotherms on AgY (56 Ag<sup>+</sup>/unit cell) and CuY (14 Cu<sup>+</sup>/unit cell) at 120°C;

Fig. 3 is a graph depicting thiophene/benzene and thiophene/n-octane breakthrough in AgY, NaY zeolite at room temperature;

Fig. 4 is a graph depicting cumulative pore volumes of sorbents used in Experiment C;

Fig. 5 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on Na-Y (Si/Al=2.43) at 120 °C and 180 °C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 6 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on Ag-Y (Si/Al=2.43) at 120°C and 180°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms; fitted curves are not shown for benzene adsorption at 180°C because the artificial crossovers to the curves for thiophene at 180°C are observed;

Fig. 7 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on Cu-Y (Si/Al=2.43) at 90°C and 120°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 8 is a graph depicting pure component equilibrium isotherms of thiophene on Ag-X (Si/Al=1.25) and Ag-Y (Si/Al=2.43) at 120°C;

Fig. 9 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on H-USY (Si/Al=195) at 90°C and 120°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 10 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on Na-ZSM-5 (Si/Al=10) at 90°C and 120°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 11 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on activated carbon (Type PCB) at 90°C and 120°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 12 is a graph depicting pure component equilibrium isotherms of benzene and thiophene on modified activated alumina (Selexsorb CDX) at 90°C and



120°C; curves are fitted with Dubinin-Astakhov (solid line) and Langmuir-Freundlich (dotted line) isotherms;

Fig. 13 is a graph comparing equilibrium adsorption isotherms of thiophene at 120°C;

Figs. 14-21 are graphs depicting various breakthrough curves;

Fig. 22 is a graph depicting pure component equilibrium isotherms for benzene and cyclohexane adsorption on H-USY at 120 and 180 °C; curves are fitted with Dubinin-Astakhov (solid lines) and Langmuir-Freundlich (dotted lines) isotherms;

Fig. 23 is a graph depicting pure component equilibrium isotherms for benzene and cyclohexane adsorption on Na-Y at 120 and 180 °C; curves are fitted with Dubinin-Astakhov (solid lines) and Langmuir-Freundlich (dotted lines) isotherms;

Fig. 24 is a graph depicting pure component equilibrium isotherms for benzene and cyclohexane adsorption on Ag-Y at 120 and 180 °C; curves are fitted with Dubinin-Astakhov (solid lines) and Langmuir-Freundlich (dotted lines) isotherms;

Fig. 25 is a graph depicting pure component equilibrium isotherms for benzene and cyclohexane adsorption on Pd-Y at 120 °C; curves are fitted with Dubinin-Astakhov (solid lines) and Langmuir-Freundlich (dotted lines) isotherms;

Fig. 26 is a graph depicting pore size distributions of Na-Y, Ag-Y, Pd-Y and H-USY;

Fig. 27 is a graph comparing experimental and GCMC simulation for adsorption of benzene on Na-Y;

Fig. 28 is a graph comparing experimental and GCMC simulation for adsorption of benzene on H-USY; and

Fig. 29 is a graph comparing experimental and GCMC simulation for adsorption of benzene on Ag-Y.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is predicated upon the unexpected and fortuitous discovery that thiophene and thiophene compounds are adsorbed slightly more selectively via  $\pi$ -complexation than is benzene. This is quite counter-intuitive, as it would be expected that benzene, having more double bonds (3) and more  $\pi$  electrons than thiophene (2 double bonds), would be more selectively adsorbed via  $\pi$ -complexation. An example of a compound having more double bonds being more selectively adsorbed than

a compound having fewer double bonds may be found in U.S. Patent No. 6,215,037, issued to Padin, Munson and Yang in 2001 and entitled, "Method for Selective Adsorption of Dienes."

Without being bound to any theory, it is believed that this counter-intuitive, slightly higher selectivity for thiophene/thiophene derivatives/compounds may be explained by the following theory. The sulfur atom in the five-member thiophene ring has more electrons than the carbons. As such, the S atom, with its available electrons and relatively strong attraction, may be aiding in the  $\pi$ -complexation bonding, thus contributing to the higher selectivity of the present sorbents for thiophenes over benzene. How much the sulfur could contribute to  $\pi$ -complexation bonding, however, is not predictable.

The present invention is a startling and useful discovery, in that the sorbents and process of the present invention adsorb more than 1 mmol/gram of thiophene at  $10^{-5}$  atm. The present inventive process utilizing sorbents which adsorb via  $\pi$ -complexation may be used to remove sulfur compounds (for example, heterocyclic diunsaturated sulfur compounds) from hydrocarbons such as liquid fuels (including, but not limited to gasoline, diesel fuels, coal and shale derived liquid fuels, methanol, and the like). Liquid fuels have a high concentration of aromatics, such as eg. benzene, and a low concentration of thiophene and thiophene compounds (in the parts-per-million (ppm)). Thus, it is one important aspect of the present invention that the inventive process adsorbs the thiophenes at least slightly more selectively than benzene.

This is a substantial advance over currently available commercial sorbents, which adsorb little, if any, thiophene or thiophene compounds at low concentrations. For example, activated carbon was recently tested by the present inventors, and was found to behave similarly to Na-Y (discussed in further detail below), in that it adsorbed very little (below 1/10 mmol/gram) benzene and thiophene at  $10^{-5}$  atm.

Without being bound to any theory, it is believed that the higher sorbent capacity of embodiments of the present invention may be due to a sorbent pretreatment method of an embodiment of the present invention wherein the sorbent is calcined at 350°C and cooled in dry atmosphere.

The present inventive process may advantageously be run at ambient temperature and pressure, which is highly desirable for a variety of reasons. It is much less energy consuming to run processes at ambient temperature and pressure. Further, conventional catalytic desulfurizing processes, processes are typically run at high temperatures, eg. 700°C, and high pressures, causing the (very expensive) catalyst to be continually deactivated. Further, the reactor size of a conventional process would need to

be exponentially increased over present reactor sizes in order to remove thiophenes lower than the currently acceptable several hundred ppm. Still further, the present inventive process may be used as a first line desulfurizing process, and/or as a clean up desulfurizing process to remove sulfur compounds missed by conventional processes, such as those processes discussed above (eg. hydrodesulfurization). It could be very useful to have the option to add the present invention as a downstream "clean up" desulfurizing process, in that it may not be necessary to revamp current refining processes upstream from the present inventive process. This could solve the cost-prohibitive problems encountered by some refiners. See Parkinson, G., (cited above).

The sorbents of the present invention, one example of which is Cu(I)Y, may be substantially fully regenerated by first air oxidation (e.g., at about 350°C), followed by auto-reduction in an inert atmosphere (e.g., at about 450°C).

The process and sorbents of the present invention may have quite significant cost benefits on the future energy picture. For example, for a full tank of gas, it is estimated that it would cost only about 70 cents to remove the sulfur from the current 350 ppm to below 5 ppm. If some blending were done, to meet the new (2006) EPA standard, then it is estimated that it would cost only about 12 cents. These costs are based on the assumption that the sorbent is disposable - no regeneration. However, it is estimated that the cost could be considerably less if the sorbent were regenerated (for example, as described above, ie. air oxidation followed by auto-reduction in inert atmosphere).

Although the process of the present invention has specifically tested Cu-Y and Ag-Y (as well as other sorbents), it is to be understood that Type X zeolites may in some cases be as good as, or better zeolites than Y zeolites, since more cations are available in X zeolites. Further, it is to be understood that other zeolites are contemplated as being within the scope of the present invention. Still further, it is to be understood that all d-block transition metals and/or their ions may be used in place of the copper or silver, as it is believed that any d-block element will form  $\pi$ -complexation bonds with thiophene and thiophene compounds. In particular, it is believed that  $\text{Ni}^{2+}$  and  $\text{Pd}^{2+}$  would be as effective as  $\text{Cu}^+$  and  $\text{Ag}^+$ . Further, the metals do not need to be ion-exchanged, but rather may be dispersed (monolayer dispersion, island dispersion, etc.) on a carrier (such as, for example, silica, alumina, etc.) by any suitable method.

In an embodiment of the present invention, the process for removing thiophene and thiophene compounds from liquid fuel comprises the step of contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed

component and a thiophene/thiophene compound-rich adsorbed component. It is to be understood that in the "thiophene/thiophene compound-rich adsorbed component" term as used herein, the thiophenes may not be the greatest amount of adsorbate. For example, in the case of liquid fuels having a very high concentration of aromatics, and a very low concentration of thiophenes, the adsorbed phase will actually contain more benzene than thiophene, because there is much more benzene than thiophene in the solution. The adsorbed phase may have thiophene/benzene at a ratio of about 1/2. However, that would be enough to advantageously purify the solution.

The adsorbent comprises any ion-exchanged zeolite, but in a preferred embodiment, the zeolite is selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof. The zeolite has exchangeable cationic sites, and at least some of the sites have d-block transition metal cation present. The preferential adsorption occurs by  $\pi$ -complexation.

In a further embodiment, the invention comprises a process for removing thiophene and thiophene compounds from liquid fuel. The method comprises the step of contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and a thiophene/thiophene compound-rich adsorbed component. The adsorbent comprises a carrier having a surface area, the carrier having a d-block transition metal compound dispersed on at least some of the surface area. The metal compound releasably retains the thiophenes. The carrier comprises a plurality of pores having a pore size greater than the effective molecular diameter of the thiophene/thiophene compounds. The method may further comprise the step of changing at least one of the pressure and temperature to thereby release the thiophene/thiophene compound-rich component from the adsorbent.

As suggested by King, chemical complexation bonds are generally stronger than van der Waals interactions (thus giving rise to higher selectivities), yet weak enough to be reversible (i.e., to be broken by simple engineering means). See, for example, King, C.J., "Separation Processes Based on Reversible Chemical Complexation," *Handbook of Separation Process Technology*, R.W. Rousseau ed., Wiley, New York, 1987, Chap. 15. Therefore, a tremendous opportunity exists for developing new sorbents (and new applications in separation and purification) by using weak chemical bonds, including various forms of complexation bonds. Based on the principles of  $\pi$ -complexation, the inventor(s) have already developed a number of new sorbents for a number of applications. These include sorbents for: (a) olefin/paraffin separations (see, for example, Yang, R.T.; Kikkinides, E. S. "New Sorbents for Olefin-

Paraffin Separations by Adsorption via  $\pi$ -Complexation," *AIChE J.*, **1995**, *41*, 509; Rege, S. U.; Padin, J.; Yang, R. T. "Olefin-Paraffin Separations by Adsorption: Equilibrium Separation by  $\pi$ -Complexation vs. Kinetic Separation," *AIChE J.*, **1998**, *44*, 799; Huang, H. Y.; Padin, J.; Yang, R. T. "Ab Initio Effective Core Potential Study of Olefin/Paraffin Separation by Adsorption via  $\pi$ -Complexation: Anion and Cation Effects on Selective Olefin Adsorption," *J. Phys. Chem. B.*, **1999**, *103*, 3206; Huang, H. Y.; Padin, J.; Yang, R. T. "Comparison of  $\pi$ -Complexations of Ethylene and Carbon Monoxide and  $\text{Cu}^+$  and  $\text{Ag}^+$ ," *Ind. Eng. Chem. Res.*, **1998**, *38*, 2720; and Padin, J.; Yang, R. T. "New Sorbents for Olefin-Paraffin Separations by Adsorption via  $\pi$ -Complexation: Synthesis and Effects of Substrates," *Chem. Eng. Sci.*, **2000**, *55*, 2607.); (b) diene/olefin separation or purification (i.e., removal of trace amounts of dienes from olefins) (see Padin, J.; Yang, R. T.; Munson, C. L. "New Sorbents for Olefin-Paraffin Separations and Olefin Purification for  $\text{C}_4$  Hydrocarbons," *Ind. Eng. Chem. Res.*, **1999**, *38*, 3614; Jarayaman, A.; Yang, R. T.; Munson, C. L.; Chinn, D. "Deactivation of  $\pi$ -Complexation Adsorbents by Hydrogen and Rejuvenation by Oxidation," *Ind. Eng. Chem. Res.*, **2001**; and Takahashi, A.; Yang, R. T.; Munson, C. L.; Chinn, D. "Cu(I)-Y Zeolite as a Superior Adsorbent for Diene/Olefin Separation," *Langmuir*, **2001**.); and (c) aromatics/aliphatics separation and purification (i.e., removal of trace amounts of aromatics from aliphatics) (see Takahashi, A.; Yang, F. H.; Yang, R. T. "Aromatics/Aliphatics Separation by Adsorption: New Sorbents for Selective Aromatics Adsorption by  $\pi$ -Complexation," *Ind. Eng. Chem. Res.*, **2000**, *39*, 3856; and Takahashi, A.; Yang, R. T. "New Adsorbents for Purification: Selective Removal of Aromatics," *AIChE J.*, submitted (2001)). For purification, vapor phase results can be applied directly to liquid phase applications. In the present invention, the inventors have used molecular orbital calculations to obtain a basic understanding for the bonding between the sorbates and sorbent surfaces, and further, to develop a methodology for predicting and designing  $\pi$ -complexation sorbents for targeted molecules (see, for example, Huang, H. Y.; Padin, J.; Yang, R. T. "Ab Initio Effective Core Potential Study of Olefin/Paraffin Separation by Adsorption via  $\pi$ -Complexation: Anion and Cation Effects on Selective Olefin Adsorption," *J. Phys. Chem. B.*, **1999**, *103*, 3206; and Huang, H. Y.; Padin, J.; Yang, R. T. "Comparison of  $\pi$ -Complexations of Ethylene and Carbon Monoxide and  $\text{Cu}^+$  and  $\text{Ag}^+$ ," *Ind. Eng. Chem. Res.*, **1998**, *38*, 2720).

In the present invention, the inventors obtained first results on new sorbents for desulfurization using  $\pi$ -complexation. CuY and AgY were the sorbents, and thiophene and benzene were used as the model system. Since NaX (i.e., 13X) or NaY is

among the best commercially available sorbents for thiophene, NaY was used as the reference for comparison.

The sulfur breakthrough curves with AgY and NaY zeolites (Figure 3), with a liquid feed of thiophene in octane, shows AgY to be an excellent sorbent.

Further experiments were run with Cu(I)Y. Surprisingly, even though the results with AgY were very good, the results with Cu(I)Y were better than those of AgY. The sorbent capacity of Cu(I)Y is much higher than that of AgY, and very pure octane was obtained for extended periods of time. The sulfur capacity of Cu(I)Y zeolite was found to be about 2.55 mmol/g (or, 21.4 wt %). This is an extremely high capacity because the experiments were removing ppm levels of sulfur.

Ag-exchanged faujasite was claimed for thiophene removal in U.S. Patent No. 4,188,285 issued to Michlmayr. In sharp contrast to the present invention, the '285 preferred temperature for adsorption was 200-350°C, and the sorbent was not dehydrated by heat-treatment prior to adsorption. Also in sharp contrast to the present invention, the '285 sulfur capacities were very low, at about 0.07-0.15 wt% for Ag-Y. In the '285 patent, the highest sulfur capacity (of 0.2 wt%) was obtained with the lowest Ag content, with USY zeolite. The '285 sorbent was apparently intended for bonding the sulfur atom with Ag. It was not intended for  $\pi$ -complexation. In contrast, the sorbents of the present invention, for example, the Cu(I)Y sorbent has a sulfur capacity > 100 times larger.

Vansant et al. in European Patent Publication No. 0 275 855 investigated Cu(II)Y for thiophene removal. In contrast to the present invention, the '855 Cu<sup>2+</sup> exchanged Y zeolite was purposely heat-treated in air (to 200-550°C) to maintain the Cu<sup>2+</sup> in the divalent state. Thus, in contrast to the present invention, in the '855 publication adsorption by  $\pi$ -complexation was not intended. The '855 publication discloses low thiophene capacities (the highest was 1.6 wt%). In sharp contrast, the thiophene capacities of the present invention were about 21.4 wt%.

Figs. 14-21 are graphs depicting various breakthrough curves.

To further illustrate the present invention, the following examples are given. It is to be understood that these examples are provided for illustrative purposes and are not to be construed as limiting the scope of the present invention.

### EXAMPLES

#### **EXPERIMENT A**

##### **Sorbent Preparation**

Cu<sup>+</sup>-Y was prepared by ion exchange of Na-Y zeolites (Si/Al=2.43, 56 Al atoms/u.c., Strem Chemical) with Cu(NO<sub>3</sub>)<sub>2</sub> followed by reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>, since Cu(I) is not soluble in water. First, as-received Na-Y was exchanged twice using excess

amounts (10-fold cation-exchange-capacity (CEC) assuming that one  $\text{Cu}^{2+}$  compensates two aluminum sites) of 0.5 M  $\text{Cu}(\text{NO}_3)_2$  at room temperature for 24 hours. After the exchange, the zeolite suspension was filtered and washed with copious amount of de-ionized water. The product was dried at 100°C overnight. Several groups have reported reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  in zeolite in He (i.e., auto-reduction, see Takahashi, A.; Yang, R. T.; Munson, C. L.; Chinn, D. "Cu(I)-Y Zeolite as a Superior Adsorbent for Diene/Olefin Separation," *Langmuir*, 2001; and Larsen, S. C.; Aylor, A.; Bell, A. T.; Reimer, J. A. "Electron Paramagnetic Resonance Studies of Copper Ion-Exchanged ZSM-5," *J. Phys. Chem.*, 1994, 98, 11533). In this study, reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  was carried out in He only at 450°C for 1 hour.  $\text{Ag}^+$  ion-exchanged Y-zeolite (Ag-Y) was prepared at room temperature for 24 h in the same manner as  $\text{Cu}^{2+}$  exchange, using 5-fold excess  $\text{AgNO}_3$  (0.1M).

Single component isotherms for benzene and thiophene were measured at 120°C using standard gravimetric methods. A Shimadzu TGA-50 automatic recording microbalance was employed. Helium (Pre-purified grade, Metro welding, 99.995%) was used as the carrier gas and was first passed through two consecutive gas-wash bottles (to ensure saturation), which contained benzene (HPLC grade, Aldrich, 99.9+%) or thiophene (Aldrich, 99+%). After diluting the concentration to the desired value by blending with additional helium, the mixture was directed into the microbalance.

#### **Molecular Orbital Computational Details**

Molecular orbital (MO) studies on the  $\pi$ -complexation bonding for benzene and sorbent surfaces had been investigated recently. See Takahashi, A.; Yang, F. H.; Yang, R. T. "Aromatics/Aliphatics Separation by Adsorption: New Sorbents for Selective Aromatics Adsorption by  $\pi$ -Complexation," *Ind. Eng. Chem. Res.*, 2000, 39, 3856. In this work, similar MO studies were extended to thiophene and sorbent surfaces. The Gaussian 94 Program in Cerius2 molecular modeling software (see Bowie, J. E., *Data Visualization in Molecular Science: Tools for Insight and Innovation*; Addison-Wesley Pub. Co.: Reading, Mass., 1995; chapter 9) from Molecular Simulation, Inc. was used for all calculations. See Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robs, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*, Gaussian, Inc., Pittsburgh, PA., 1995. MO calculations for thiophene and sorbent surfaces were performed at the Hartree-Fock (HF) and density functional theory (DFT) level using

effective core potentials (ECPs). See Hay, P. J.; Wadt, W.R. "Ab Initio Effective Core Potential for Molecular Calculations. Potentials for the Transition Metals Atoms Sc to Hg," *J. Chem. Phys.* **1985**, *82*, 270; Wadt, W. R.; Hay, P. J. "Ab Initio Effective Core Potential for Molecular Calculations: Potentials for Main Group Elements Na to Bi," *J. Chem. Phys.* **1985**, *92*, 284; and Hay, P. J.; Wadt, W. R. "Ab Initio Effective Core Potential for Molecular Calculations: Potentials for K to Au Including the outermost core orbitals," *J. Chem. Phys.* **1985**, *82*, 299.

The LanL2DZ basis set (see Russo, T. V.; Martin, R. L.; Hay, P. J. "Effective Core Potentials for DFT Calculations," *J. Phys. Chem.* **1995**, *99*, 17085) is a double- $\zeta$  basis set containing ECP representations of electrons near the nuclei for post-third-row atoms. The reliability of this basis set has been confirmed by the accuracy of calculation results as compared with experimental data. Therefore, the LanL2DZ basis set was employed for both geometry optimization and natural bond orbital (NBO) analysis.

The restricted Hartree-Fock (RHF) theory at the LanL2DZ level basis set was used to determine the geometries and the bonding energies of thiophene on AgCl and CuCl. The simplest models with only a single metal chloride interacting with a thiophene molecule were chosen for  $\pi$ -complexation studies. The optimized structures were then used for bond energy calculations according to the following expression:

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{adsorbent}} - E_{\text{adsorbent-adsorbate}} \quad (1)$$

where  $E_{\text{adsorbate}}$  is the total energy of thiophene,  $E_{\text{adsorbent}}$  is the total energy of the bare adsorbent, i.e. the metal chloride, and  $E_{\text{adsorbent-adsorbate}}$  is the total energy of the adsorbate/adsorbent system. A higher value of  $E_{\text{ads}}$  corresponds to a stronger adsorption.

**Natural Bond Orbital (NBO)**

The optimized structures were also used for NBO analysis at the B3LYP/LanL2DZ level. The B3LYP (see Becke, A. D. "Density Functional Thermochemistry. III. The Role of Exact Exchanges," *J. Chem. Phys.* **1993**, *98*, 5648) approach is one of the most useful self-consistent hybrid (SCH) approaches (see Becke, A. D.; "A New Mixing of Hartree-Fock and Local Density-Functional Theories," *J. Chem. Phys.* **1993**, *98*, 1372), it is Beck's 3-parameter nonlocal exchange functional (see Becke, A. D.; "Density-Functional Thermochemistry. II. The Effect of the Perdew-Wang generalized-gradient correlation correction," *J. Chem. Phys.* **1992**, *97*, 9173) with nonlocal correlation functional of Lee, Yang and Parr. See Lee, C.; Yang, W.; Parr, R.G. "Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density," *Phys. Rev.*, **1988**, *B37*, 785.



The NBO analysis performs population analysis that pertains to localized wave-function properties. It gives a better description of the electron distribution in compounds of high ionic character, such as those containing metal atoms. See Reed, A. E.; Weinstock, R.B.; Weinhold, F. "Natural Population Analysis," *J. Chem. Phys.* **1985**, *83* (2), 735. It is known to be sensitive for calculating localized weak interactions, such as charge transfer, hydrogen bonding and weak chemisorption. Therefore, the NBO program (Glendening, E. D.; Reed, A. E.; Carpenter, J. E., Weinhold, F. *NBO Version 3.1*, 1995) was used for studying the electron density distribution of the adsorption system.

### Results and Discussion

For purification, as the inventors have shown for the removal of ppm levels of dienes from olefins (Takahashi, A.; Yang, F. H.; Yang, R. T. "Aromatics/Aliphatics Separation by Adsorption: New Sorbents for Selective Aromatics Adsorption by  $\pi$ -Complexation," *Ind. Eng. Chem. Res.*, **2000**, *39*, 3856; and Takahashi, A.; Yang, R. T. "New Adsorbents for Purification: Selective Removal of Aromatics," *AIChE J.*, submitted **2001**), one parameter is the separation factor; and the separation factor should be evaluated at *low* concentrations of the solute but at *high* concentrations of the solvent. In other words, the capacity for the dilute solute (at ppm level) is an important factor in determining the purification. The separation factor ( $\alpha$ ) is given by:

$$\alpha_{12} = X_1 Y_2 / (X_2 Y_1) \quad (2)$$

where X and Y are mole fractions in the adsorbed and fluid phases, respectively. In our case, component 1 is thiophene and component 2 is benzene. Hence, the ability of the sorbent for purification depends on the amount of *thiophene* adsorbed at the *ppm levels*.

Figure 1 shows the equilibrium isotherms of benzene and thiophene on NaY at 120°C. NaY does not have a selectivity for thiophene; however, it adsorbs both benzene and thiophene quite strongly, as evidenced by the still measurable amounts adsorbed at partial pressures as low as 10-100 ppm of 1 atm. As expected, a fixed-bed adsorber experiment using NaY would yield a breakthrough curve (Yang, R. T. *Gas Separation by Adsorption Processes*, Butterworth, Boston, **1987**, Imperial College Press, London, **1997**), as seen in the literature (Salem, A. S. H.; Hamid, H. S. "Removal of Sulfur Compounds from Naphtha Solutions Using Solid Adsorbents," *Chem. Eng. Tech.*, **1997**, *20*, 342). The data were fitted by the Langmuir-Freundlich isotherm (Takahashi, A.; Yang, R.T.; Munson, C.L.; Chinn, D. "Cu(I)-Y Zeolite as a Superior Adsorbent for Diene/Olefin Separation," *Langmuir*, **2001**; Takahashi, A.; Yang, F. H.; Yang, R. T.

"Aromatics/Aliphatics Separation by Adsorption: New Sorbents for Selective Aromatics Adsorption by  $\pi$ -Complexation," *Ind. Eng. Chem. Res.*, **2000**, *39*, 3856; and Takahashi, A.; Yang, R. T. "New Adsorbents for Purification: Selective Removal of Aromatics," *AIChE J.*, submitted **2001**), as shown by the lines in the figure.

Figure 2 shows the isotherms of benzene and thiophene on AgY and CuY. Note that: (a) compared with NaY, AgY and CuY adsorb both thiophene and benzene more strongly at below  $10^{-3}$  atm, due to  $\pi$ -complexation; and (b) on a per-cation basis,  $\text{Cu}^+$  shows stronger interactions than  $\text{Ag}^+$ . Compared with Figure 1, these sorbents adsorbed significantly more thiophene and benzene than NaY at pressures below  $10^{-3}$  atm, and nearly the same amounts at high partial pressures. This result was a clear indication of  $\pi$ -complexation with  $\text{Ag}^+$  and  $\text{Cu}^+$ ;  $\text{Na}^+$  could not form  $\pi$ -complexation bonds. From the data in Figures 1 and 2, the separation factors were calculated using mixed Langmuir-Freundlich isotherms (Taka), and are shown in Table 1. However, these separation factors did not reflect the relative strengths of  $\pi$ -complexation between  $\text{Cu}^+$  and  $\text{Ag}^+$  because the  $\text{Cu}^+$  exchange was not complete. Nonetheless, the large separation factors indicate that AgY and CuY are excellent sorbents for purification purposes.

**Table 1. Separation factors of thiophene over benzene estimated from pure-component isotherms by extended Langmuir-Freundlich Equation at the pressure of  $3 \times 10^{-5}$  atm for thiophene and 1 atm for benzene.**

| Adsorbent         | Ag-Y | Cu-Y | Na-Y |
|-------------------|------|------|------|
| Separation Factor | 2800 | 50   | 0.10 |

The neutron activation analyses of the sorbent samples showed that the  $\text{Ag}^+$  exchange was 100% but the  $\text{Cu}^+$  exchange was only 23%. On a per-cation basis, the  $\pi$ -complexation with  $\text{Cu}^+$  was stronger than that with  $\text{Ag}^+$ . This was indeed confirmed by our molecular orbital calculations, as will be discussed. To understand the relative strengths of  $\pi$ -complexation between  $\text{Ag}^+$  and  $\text{Cu}^+$ , the thiophene adsorption amounts at  $2 \times 10^{-5}$  atm were normalized by  $\text{Ag}^+$  or  $\text{Cu}^+$  content, and the results are shown in Table 2. It is seen that  $\text{Cu}^+$  could adsorb higher thiophene adsorption amounts per cation. In fact, 0.92 thiophene molecule per  $\text{Cu}^+$  was obtained at  $2 \times 10^{-5}$  atm at  $120^\circ\text{C}$ . This amount was due to  $\text{Cu}^+$  since the amount adsorbed by NaY at the same pressure was negligible. At the same pressure, only 0.42 thiophene/ $\text{Ag}^+$  was obtained. This result indicated strong  $\pi$ -complexation bonds between both  $\text{Cu}^+$  and  $\text{Ag}^+$ , and that the bond with  $\text{Cu}^+$  was

stronger. Further work is in progress to increase the  $\text{Cu}^+$  contents on various X/Y and other zeolites and the results will be reported shortly.

**Table 2. Thiophene adsorption amount normalized by cation content (thiophene/cation).**

| Adsorbent                                   | Ag-Y          | Cu-Y          |
|---|---------------|---------------|
| Cation for $\pi$ -complexation              | $\text{Ag}^+$ | $\text{Cu}^+$ |
| Cation Content in Zeolite (wt%)             | 38.2          | 8.29          |
| Amount Adsorbed (thiophene molecule/cation) | 0.42          | 0.92          |

The heats of adsorption for  $\pi$ -complexation were estimated by taking the values at low loadings, and they were obtained from the temperature dependence of the isotherms at low pressures. These values are given in Table 3.

**Table 3. Heats of adsorption (kcal/mol) for  $\pi$ -complexation.**

| Zeolite | Thiophene | Benzene |
|---------|-----------|---------|
| Cu(I)-Y | 22.3      | 21.8    |
| Ag-Y    | 21.4      | 20.1    |

#### **Bond Energies, Geometries and NBO results**

The energies of adsorption calculated using equation 1 for thiophene and benzene are summarized in Table 4.

**Table 4. Summary of energies of adsorption for thiophene and benzene in kcal/mol.**

| MCI  | $E_{\text{ads}}$ (Thiophene) | $E_{\text{ads}}$ (Benzene) |
|------|------------------------------|----------------------------|
| CuCl | 13.5                         | 12.4                       |
| AgCl | 9.0                          | 8.6                        |

The theoretical calculations indicate that the  $\pi$ -complexation strengths follow the order  $\text{CuCl} > \text{AgCl}$  and more importantly, thiophene > benzene. This trend is in agreement with the experimental data, in Table 3. Chloride was used as the anion in the theoretical calculations, while zeolite framework was the anion in the experiment. It is known from

our previous work that the anion has a large effect on the  $\pi$ -complexation bonds. See, for example, Huang, H.Y.; Padin, J.; Yang, R. T. "Ab Initio Effective Core Potential Study of Olefin/Paraffin Separation by Adsorption via  $\pi$ -Complexation: Anion and Cation Effects on Selective Olefin Adsorption," *J. Phys. Chem. B.*, **1999**, *103*, 3206; and Huang, H. Y.; Padin, J.; Yang, R. T. "Comparison of  $\pi$ -Complexations of Ethylene and Carbon Monoxide and  $\text{Cu}^+$  and  $\text{Ag}^+$ ," *Ind. Eng. Chem. Res.*, **1998**, *38*, 2720. In the optimized structures of thiophene-MCl complexes, the distance between the thiophene molecule and Cu ion is about 0.3 Å shorter than that of thiophene and Ag ion. The NBO analysis is summarized in Tables 5 and 6. There is some donation of electron charges from the  $\pi$ -orbital of thiophene to the vacant s orbital of metals known as  $\sigma$  donation and, simultaneously, back donation of electron charges from the d orbitals of metals to  $\pi^*$  orbital of thiophene or  $\pi$  back-donation. The  $\pi$  back-donation appears to be important in all cases. The charge transfer results again confirmed the experimental data that the relative strengths of the  $\pi$ -complexation bonds follow the order: thiophene > benzene and  $\text{Cu}^+ > \text{Ag}^+$ .

**Table 5. Summary of NBO analysis\* of  $\pi$ -complexation between thiophene and MCl.**

| MCl  | C→M interaction<br>( $\sigma$ donation)<br>$q_1$ | M→C interaction<br>(d - $\pi^*$ backdonation)<br>$q_2$ | Net Change<br>$q_1 + q_2$ |
|------|--|--|---------------------------|
| CuCl | 0.037  | -0.022   | 0.015                     |
| AgCl | 0.022  | -0.014   | 0.008                     |

\*  $q_1$  is the amount of electron population change in valence s orbitals of the metal, and  $q_2$  is the total amount of electron population decrease in valence d orbitals of the metal.

**Table 6. Summary of NBO analysis\* of  $\pi$ -complexation between benzene and MCl.**

| MCl  | C→M interaction<br>( $\sigma$ donation)<br>$q_1$ | M→C interaction<br>(d - $\pi^*$ backdonation)<br>$q_2$ | Net Change<br>$q_1 + q_2$ |
|------|--|--|---------------------------|
| CuCl | 0.011  | -0.013   | -0.002                    |
| AgCl | 0.003  | -0.007   | -0.004                    |

\*  $q_1$  is the amount of electron population change in valence s orbitals of the metal, and  $q_2$  is the total amount of electron population decrease in valence d orbitals of the metal.

## EXPERIMENT B

### Thiophene Removal Using Sodium and Silver Cation in Faujasite Zeolites

Work has been done on different adsorbents to remove sulfur from mixtures, such as, for example, thiophene from benzene or n-octane based solutions.

These adsorbents include sodium and silver forms of faujasite type zeolites, particularly, Y type zeolites. Initial studies were done for the case of an inlet concentration of 2000 ppmw of thiophene in either benzene or n-octane.

### Sorbent Preparation

Sodium Y Zeolite powder was obtained from Strem Chemicals. Silver Y Zeolite was obtained by ion exchanging NaY at room temperature. The solution was prepared using a silver nitrate salt and deionized water (~0.2 M). A 4-fold excess amount of silver was used to ensure exchange completion. After ion exchanging for 48 hours, the adsorbent was recovered by filtration and washed with large amounts of deionized water. Drying was performed at room temperature.

### Breakthrough Experiments

Breakthrough experiments were performed in a custom made quartz reactor equipped with a glass frit. The adsorbent was loaded inside the reactor (usually 1 or 2 grams) and activated *in situ* under a helium atmosphere at 350°C for 24 hrs. The adsorbent was then cooled down to room temperature. At this point, the sorbent was wetted by pouring down sulfur free solvent (benzene or n-octane) for about 30 minutes. This stream was then changed to one containing 2000 ppmw thiophene. Samples were collected at different time intervals, and the thiophene outlet concentration was analyzed using a GC unit equipped with a polar column at 65°C.

### Preliminary Results

Figure 3 shows breakthrough curves for thiophene in either benzene or n-octane in sodium or silver forms of Y Zeolite.

*Thiophene adsorption amounts after saturation.*

|          | NaY                        | AgY   |
|----------|----------------------------|-------|
| Solvent  | Saturation Amount (mmol/g) |       |
| Benzene  | 0.102                      | 0.171 |
| n-Octane | ----                       | 0.898 |

Integration of the area above the curves yield the adsorption saturation amounts presented in the table shown above. For the case of thiophene/benzene

mixtures, the calculated thiophene adsorption amounts are not that high. Very recent single component vapor phase adsorption experiments have shown that NaY and AgY may adsorb benzene and thiophene in similar quantities. Thus, benzene may compete for many of the adsorption sites, perhaps leaving thiophene with fewer available sites. However, despite the possibility of competitive adsorption, the presence of silver cations results in an increase in some adsorption capacity. For the case of thiophene/n-Octane mixtures, AgY Zeolite shows great selectivity towards thiophene. Without being bound to any theory, it is believed that this indicates that the interaction between the silver cations and the thiophene molecules is higher than that of n-Octane molecules.

### EXPERIMENT C

In this experiment, the known commercial sorbents such as Na-Y, Na-ZSM5, H-USY, activated carbon and activated alumina (Alcoa Selexsorb) were included, and a direct comparison was made with Cu-Y and Ag-Y which were the sorbents with  $\pi$ -complexation capability. Thiophene and benzene were used as the model system for desulfurization.

#### Sorbent preparation

Various kinds of sorbents were investigated in this work. Four as-received sorbents: Na-type Y-zeolite (Na-Y, Si/Al=2.43, 56 Al atoms/unit cell, Strem Chemical), H-type ultra-stable Y-zeolite (H-USY, Si/Al=195, 0.98 Al atoms/u.c., HSZ-390HUA, TOSOH Corporation), activated carbon (Type PCB, Calgon Carbon Corporation) and modified activated alumina (Selexsorb CDX, Alcoa Industrial Chemical), were used in this study. According to the product datasheets, Selexsorb CDX is formulated for adsorption of sulfur-based molecules, nitrogen-based molecules, and oxygenated hydrocarbon molecules. Na-Y and H-USY were in powder form (binderless). Since activated carbon was in granular form and activated alumina was in pellet form, they were crushed into powder form for evaluation.

$\text{Cu}^+$ -Y and Ag-Y were prepared as in Experiment A, above. 13X (Si/Al=1.25, Linde, lot#945084060002) was used for the preparation of Cu-X (10 fold CEC solution of  $\text{Cu}(\text{NO}_3)_2$ , ion-exchanged at 65 °C for 24 hrs, three times) and Ag-X (5-fold CEC solution of  $\text{AgNO}_3$ , ion-exchanged at RT for 24 hrs, twice). Na-type ZSM-5

(Na-ZSM-5) was prepared at room temperature by  $\text{Na}^+$ -exchange of  $\text{NH}_4$ -ZSM-5 (Si/Al=10, SM-24, ALSI-PENTA Zeolite GmbH).

#### **Isotherm and uptake rate measurements**

The objective of this study is to compare the strength of adsorptive interaction between adsorbents and thiophene/benzene. Extremely low partial pressures at less than  $10^{-5}$  atm would be necessary to meet this objective if isotherms were measured at ambient temperature, because the isotherms at ambient temperature are fairly flat and are difficult to compare each other. However, it is very difficult to obtain and control such low partial pressures experimentally. Therefore, single component isotherms for benzene and thiophene were measured at 90°C, 120°C and 180 °C using standard gravimetric methods. A Shimadzu TGA-50 automatic recording microbalance was employed. Helium (Pre-purified grade, Metro welding, 99.995%) was used as the carrier gas and was first passed through two consecutive gas-wash bottles (to ensure saturation), which contained benzene (HPLC grade, Aldrich, 99.9+%) or thiophene (Aldrich, 99+%). After diluting the concentration to the desired value by blending with additional helium, the mixture was directed into the microbalance.

Isothermic heats of adsorption were calculated using the Clausius-Clapeyron equation from isotherms at different temperatures. Nitrogen isotherms at 77K measured with a Micromeritics ASAP 2010 system were used for pore size distribution and pore volume determination. Pore size distributions were calculated with Horvath-Kawazoe equation. See Horvath, G., and K. Kawazoe, "Method for Calculation of Effective Pore Size Distribution in Molecular Sieve Carbon," *J. Chem. Eng. Japan*, **1983**, 16, 470; Saito, A, and H. C. Foley, "Curvature and Parametric Sensitivity in Models for Adsorption in Micropore," *AIChE J*, **1991**, 37, 429; and Cheng, L. S., and R.T. Yang, "Improved Horvath-Kawazoe Equations Including Spherical Pore Models for Calculating Micropore Size Distribution," *Chem. Eng. Sci.* **1994**, 49, 2599. Slit pore model was used for activated carbon, and cylindrical pore model was used for ZSM-5 and activated alumina, while spherical pore model was applied to Y-zeolites and X-zeolites. As for the parameters for H-K equation such as polarizability, magnetic susceptibility, density, etc., default values in Micromeritics ASAP system were used for the calculation of pore sizes. See "Accelerated Surface Area and Porosimetry System Operator's Manual V3.02,"

Micromeritics Instrument Corp., (1997). The diffusion time constants,  $D/r^2$  ( $s^{-1}$ ), were calculated from the uptake rates. See Yeh, Y. T., "Diffusion and Adsorption of Gases in Molecular Sieves," Ph.D. Dissertation, University of New York at Buffalo, Buffalo, New York, 1989. In this experiment, short time region (up to 30 % uptake) and spherical adsorbent model were used.

### **Chemical Analysis**

The compositions of Cu-Y and Ag-Y were characterized using neutron activation analysis (NAA) in the research nuclear reactor of the Phoenix Memorial Laboratory at the University of Michigan. The sample was irradiated sequentially for one minute at a core-face location with an average thermal neutron flux of  $2 \times 10^{12}$  n/cm<sup>2</sup>/s. Two separate gamma-ray spectra were then collected for each sample with a high resolution germanium detector: one after 13-minute decay to determine the concentrations of Al, Ag and Cu, and a second after a 1 hour and 56-minute decay to analyze for Na. Gamma energy lines at 1779 keV, 632.99 keV, 1039.20 keV and 1368.6 keV were used for the determination of Al, Ag, Cu and Na concentration, respectively.

Molecular Orbital Computational Details and Natural Bond Orbitals are as described in Experiment A above.

### **Models for Ag-Zeolite (AgZ) and Cu-Zeolite (CuZ)**

The zeolite models selected for this study are similar to the ones used by Chen and Yang (see Chen, N. and R. T. Yang, "Ab Initio Molecular Orbital Study of Adsorption of Oxygen, Nitrogen, and Ethylene on Silver-Zeolite and Silver Halides," *Ind. Eng. Chem. Res.* 1996, 35, 4020), with the molecular formula of  $(HO)_3Si-O-Al(OH)_3$ , and the cation  $Ag^+$  or  $Cu^+$  sits 2 – 3 Å above the bridging oxygen between Si and Al. This is a good cluster model representing the chemistry of a univalent cation bonded on site II (SII) of the faujasite framework (Z). Once the optimized structures of AgZ and CuZ are obtained at the B3LYP/LanL2DZ level, then a molecule of thiophene ( $C_4H_4S$ ) or benzene ( $C_6H_6$ ) is added onto the cation of the zeolite model, and the resulting structure is further optimized at the B3LYP/LanL2DZ level.



## Results and Discussion

**Characterization of sorbents.** Neutron activation analysis showed that Ag/Al and Na/Al ratios in Ag-Y were 1.13 and 0.01, respectively. This is because  $\text{Ag}^+$  is known to have higher selectivity to cation sites in zeolites compared to  $\text{Na}^+$ . See Breck, D.W. *Zeolite Molecular Sieves: Structure, Chemistry and Use*; Wiley: New York, 1974. More than 100% Ag ion-exchange ratio was obtained in Ag-Y, because some Ag ions were located outside the charge-compensating sites. On the other hand, the Al, Cu, and Na contents in Cu-Y were  $6.10 \pm 0.25$  wt%,  $6.65 \pm 0.05$  wt%, and  $1.50 \pm 0.12$  wt%, respectively. This means that the Cu/Al molar ratio was 0.463, and the Na/Al ratio was 0.289, indicating less selectivity than  $\text{Ag}^+$ . Therefore, Cu ion-exchange for X-zeolite was carried out three times at 65 °C (instead of twice at RT for Cu-Y) for 24 hrs to enhance the ion-exchange.

Figure 4 shows the comparison of the cumulative pore volumes of the sorbents used. Activated carbon has the largest pore volume with small pores, while Na-ZSM-5 has the smallest pore volume. Selexsorb CDX also shows small pores. Because silver is heavier than copper and the silver content in Ag-Y (Ag/Al=1.13) was more than copper content in Cu-Y (Cu/Al = 0.463), the density of Ag-Y was higher by 36% ( $\text{Na}_{0.084}\text{Cu}_{0.135}\text{Al}_{0.292}\text{Si}_{0.708}\text{O}_2$ ; MW = 70.27 vs.  $\text{Ag}_{0.330}\text{Al}_{0.292}\text{Si}_{0.708}\text{O}_2$ ; MW = 95.36). Consequently, the pore volume of Ag-Y was about 25 % smaller than that of Cu-Y.

**Benzene/Thiophene adsorption isotherms: Na-Y.** Figure 5 shows the equilibrium isotherms of benzene and thiophene on Na-Y at 120°C and 180°C. The data were fitted by the Langmuir-Freundlich and Dubinin-Astakhov isotherms (see Padin, J.; Yang, R. T.; Munson, C. L., "New Sorbents for Olefin-Paraffin Separations and Olefin Purification for C<sub>4</sub> Hydrocarbons," *Ind. Eng. Chem. Res.*, **1999**, 38, 3614; Jayaraman, A; Yang, R. T.; Munson, C. L.; Chinn, D., "Deactivation of  $\pi$ -Complexation Adsorbents by Hydrogen and Rejuvenation by Oxidation," *Ind. Eng. Chem. Res.*, **2001**, 40, 4370; Takahashi, A.; Yang, R. T.; Munson, C. L.; Chinn, D., "Cu(I)-Y Zeolite as a Superior Adsorbent for Diene/Olefin Separation," *Langmuir*, **2001**, 17, 8405; Takahashi, A.; Yang, F. H.; Yang, R. T., "Aromatics/Aliphatics Separation by Adsorption: New Sorbents for Selective Aromatics Adsorption by  $\pi$ -Complexation," *Ind. Eng. Chem. Res.*, **2000**, 39, 3856; and Takahashi, A.; Yang, R. T., "New Adsorbents for Purification:

Selective Removal of Aromatics," *AIChE J.*, submitted (2001)), which are shown by the lines in Figure 5. Barthomeuf and Ha measured benzene adsorption on NaH-Y (Si/Al=2.43, 81%Na) at 172 °C. See, Barthomeuf, D. and Ha, B.-K., "Adsorption of Benzene and Cyclohexane on Faujasite-type Zeolites, Part-1, Thermodynamics Properties at Low Coverage," *J. Chem. Soc., Faraday Trans. 1*, 1973, 69, 2147. Their isotherm and calculated heat of adsorption agreed with the data shown in Figure 5 very well, substantially ensuring the accuracy of the isotherms in this work. More benzene was adsorbed on Na-Y than thiophene at pressures lower than  $10^{-2}$  atm. This result indicated that the contribution of the higher polarizability of benzene ( $10.3 \times 10^{-24}$  cm<sup>3</sup> for benzene vs.  $9.7 \times 10^{-24}$  cm<sup>3</sup> for thiophene) was larger than the contribution of the dipole moment (0 debye in benzene vs. 0.55 debye in thiophene) and lower magnetic susceptibility ( $9.1 \times 10^{-29}$  cm<sup>3</sup>/molecules for benzene vs.  $9.5 \times 10^{-29}$  cm<sup>3</sup>/molecules for thiophene). At higher pressures over  $1 \times 10^{-2}$  atm, the benzene adsorption amount became smaller owing to the larger molar volume of benzene than thiophene. Na-Y does not have a selectivity for thiophene; however, it adsorbs both benzene and thiophene quite strongly, as evidenced by the still measurable amounts adsorbed at partial pressures as low as  $10^{-4}$  to  $10^{-3}$  atm.

**Ag-Y and Cu-Y.** Figure 6 and Figure 7 show the isotherms of benzene and thiophene on Ag-Y and Cu-Y. Compared with Figure 5, these sorbents adsorbed significantly more thiophene/benzene than Na-Y at pressures below  $10^{-3}$  atm, and nearly the same amounts at high partial pressures. This result was a clear indication of  $\pi$ -complexation with Ag<sup>+</sup> and Cu<sup>+</sup>; since Na<sup>+</sup> could not form  $\pi$ -complexation bonds. However, the difference in the amounts of thiophene/benzene adsorbed did not reflect the relative strengths of  $\pi$ -complexation between Cu<sup>+</sup> and Ag<sup>+</sup> because the Cu<sup>+</sup> exchange was not complete. The neutron activation analyses of the sorbent samples showed that the Ag<sup>+</sup> exchange was 100% but the Cu<sup>+</sup> exchange was only 46%. According to the EPR analysis (described in Takahashi, A., Yang, R. T., Munson, C. L. and Chinn, D., "Cu(I)-Y Zeolite as a Superior Adsorbent for Diene/Olefin Separation," *Langmuir*, 2001, 17, 8405), only about a half of the Cu<sup>2+</sup> was auto-reduced to Cu<sup>+</sup> after our heat treatment at 450°C for 1 hr in He. On a per-cation basis, the  $\pi$ -complexation with Cu<sup>+</sup> was stronger than that with Ag<sup>+</sup>. This was indeed confirmed by our molecular orbital calculations, as will be discussed. To understand the relative strengths of  $\pi$ -complexation between Ag<sup>+</sup>

and  $\text{Cu}^+$ , the thiophene adsorption amounts at  $2 \times 10^{-5}$  atm were normalized by  $\text{Ag}^+$  or  $\text{Cu}^+$  content, and the results are shown in Table 7. It is seen that  $\text{Cu}^+$  could adsorb higher thiophene adsorption amounts per cation. In fact, 0.92 thiophene molecule per  $\text{Cu}^+$  was obtained at  $2 \times 10^{-5}$  atm at  $120^\circ\text{C}$ . This amount was due to  $\text{Cu}^+$  since the amount adsorbed by NaY at the same pressure was negligible. At the same pressure, only 0.42 thiophene/ $\text{Ag}^+$  was obtained. This result indicated strong  $\pi$ -complexation bonds between both  $\text{Cu}^+$  and  $\text{Ag}^+$ , and that the bond with  $\text{Cu}^+$  was stronger.

The vapor-phase isotherms of benzene/thiophene on Cu-Y and Ag-Y were not completely reversible within a practical time scale (1 hours to 3 hours), because of relatively strong interaction. However, the bond energies are of the order of 20 kcal/mol, which are weak enough so a substantial fraction of the adsorbed molecules are desorbed in a short period of time. For practical application, thermal desorption or displacement desorption may be a desirable option.

**Cu-X.** In order to increase the  $\text{Cu}^+$  content in the faujasite structure, an X-zeolite ( $\text{Si}/\text{Al} = 1.25$ ) was ion-exchanged with  $\text{Cu}(\text{NO}_3)_2$ . Cu-X was considered to be promising, since larger amounts of  $\text{Cu}^+$  can be present in the structure of zeolite, especially at SIII sites. The color of Cu-X powder after ion-exchange (before auto-reduction) was bluer than that of Cu-Y, suggesting that more  $\text{Cu}^{2+}$  was contained in X-zeolite than Cu-Y. For faujasite-type zeolites, the cations are designated as SI (the center of hexagonal prism), SI' (opposite SI but located in the cubooctahedron), SII (single six-ring in the supercage), SII' (opposite SII but inside the cubooctahedron), and SIII (near the four-ring windows in the supercage). See Yang, R. T. *Gas Separation by Adsorption Processes*, Butterworth, Boston, 1987, Imperial College Press, London, 1997; and Hutson, N. D.; Reisner, B. A.; Yang, R. T.; Toby, B. H., "Silver Ion-Exchanged Zeolites Y, X, and Low-Silica X: Observations of Thermally Induced Cation/Cluster Migration and the Resulting Effects on the Equilibrium Adsorption of Nitrogen," *Chem. Mater.* 2000, 12, 3020. The cations at SI, SI' and SII' sites are not exposed to the supercage and are shielded by framework oxygen. They cannot interact with molecules inside the supercages directly. Only SII and SIII sites are exposed to the supercage and can interact with molecules inside the supercage. Because Y-zeolite ( $\text{Si}/\text{Al}=2.43$ ) does not have the SIII cation sites, it is believed that only cations at SII site are responsible for the

thiophene/benzene adsorption. On the other hand, X-zeolite (Si/Al=1.25) have a certain amount of SIII sites, based on the results on Ag-X. This additional  $\text{Cu}^+$  located at SIII site should enhance the adsorption amount. However, unfortunately, it was found that Cu-X (Si/Al=1.25) was not stable at temperatures over 200°C, and the pore volume was decreased by 60 %. The color of the powder was changed from light blue to dark greenish gray after heating at 200 °C for 1 hr in vacuum. As a result, thiophene adsorption amount on Cu-X after 450 °C auto-reduction was considerably smaller than that on Cu-Y (Isotherms were not shown). To alleviate the destruction of Cu-X structure, the heating rate to 450 °C was reduced to 0.5°C/min and 2°C/min (instead of 10 °C/min ), but little improvement was observed. Although the reason for poor stability is not clear yet, copper cations were responsible for this phenomenon, because Ag-X, which will be discussed next, did not show any degradation of pore structure. It was reported that Nickel exchanged A-zeolite was unstable and lost its crystal structure at a temperature above 70 °C. See Breck, D.W., *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley: New York, 1974. The thermal instability of nickel exchanged A-zeolite was interpreted in terms of a ligand-field effect. After dehydration octahedral coordination for the nickel cation is not favored in the zeolite structure. A similar phenomenon might be occurred in copper exchanged X-zeolite.

**Ag-X.** Thiophene adsorption performance on Ag-X was also examined to understand the effect of additional  $\text{Ag}^+$  at SIII sites. Thiophene adsorption amounts on Ag-Y and Ag-X at 120°C were compared in Figure 8. Contrary to our expectation, Ag-X adsorbed less thiophene than Ag-Y on a per weight basis. However, since Ag-Y and Ag-X have different densities due to their different compositions, the adsorption amounts of thiophene were nearly the same based on per unit cell of faujasite (i.e., about 25 thiophene molecules/u.c. at  $2.3 \times 10^{-5}$  atm and 36 – 40 thiophene molecules/u.c at  $1.8 \times 10^{-2}$  atm for both Ag-Y and Ag-X). The reason for the ineffectiveness of extra  $\text{Ag}^+$  at SIII site in Ag-X is not known. The thiophene adsorption amounts were also examined from the viewpoint of zeolite pore volume and liquid thiophene volume. The molar density of liquid thiophene is calculated to be 83 cc/mol at 120 °C. See Doong, S. J.; Yang, R. T., "A Simple Potential-Theory Model for Predicting Mixed-Gas Adsorption," *Ind. Eng. Chem. Res.* 1988, 27, 630. 1.5 mmol thiophene adsorbed per gram of Ag-Y at  $2.3 \times 10^{-5}$

atm corresponded to 0.125 cc liquid thiophene per gram of Ag-Y. The thiophene liquid volume of 0.125 cc was nearly one half of pore volume of Ag-Y (0.24cc/g as shown in Figure 4), suggesting that one half of the pore was filled with thiophene. Therefore, it does seem likely that the cavity of Ag-X was filled with thiophene even at  $2.3 \times 10^{-5}$  atm and only a small amount could be further adsorbed at higher pressures. One possible reason for the relatively low amounts in Ag-X is that thiophene molecules adsorbed could be located at positions near more than one silver cations at both SII and SIII sites simultaneously, so that no improvement in adsorbed amount was observed.

Silver in Ag-X is known to form silver cluster at elevated temperature. See Sun, T. and K. Seff, "Silver Clusters and Chemistry in Zeolites," *Chem. Rev.* 1994, 94, 857. Hutson et al. showed that nitrogen adsorption capacity on Ag ion-exchanged low-silica X-zeolite (Si/Al = 1) was enhanced by heating in vacuum at 450°C for more than 4 hours. This enhancement was explained by thermally induced Ag cation and/or cluster migration using Rietvelt refinement of neutron powder diffraction data. The thiophene adsorption isotherm on Ag-X(Si/Al = 1.25) after 450 °C for 4 hours is also shown in Figure 5. No enhancement was observed for thiophene adsorption on Ag-X(Si/Al = 1.25).

**H-USY.** Thiophene and benzene isotherms on H-USY(Si/Al = 195) are shown in Figure 9. The interaction between thiophene/benzene and high-silica H-USY was very weak. Neither thiophene nor benzene was adsorbed at pressures lower than  $1 \times 10^{-3}$  atm. Adsorbed amounts were substantially smaller than Na-Y even at  $2 \times 10^{-2}$  atm. These results are clearly due to the strong interactions between the cations in zeolite and the thiophene or benzene molecule.

**Na-ZSM-5.** As stated above, several groups used Na-ZSM-5 for thiophene/benzene purification and showed that Na-ZSM-5 could remove thiophene impurities from benzene in their fixed bed breakthrough experiments. Figure 10 shows isotherms on Na-ZSM-5. Although thiophene and benzene isotherms turned out to be virtually the same on Na-ZSM-5, it may be important to note that thiophene isotherms were fairly flat over the pressure range in the application of purification. This small difference of adsorbed amounts at  $3 \times 10^{-5}$  atm and  $2 \times 10^{-2}$  atm was preferable for the purification of benzene by removal of thiophene, which will be discussed below. One

disadvantage of Na-ZSM-5 was small adsorption capacity owing to the small pore volume, as clearly seen in Figure 4.

**Activated carbon and modified activated alumina.** The thiophene and benzene adsorption isotherms on activated carbon (Type PCB) and modified activated alumina (Selexsorb CDX) are shown in Figure 11 and Figure 12. PCB activated carbon is commercially designated for use in liquid phase or vapor phase applications such as recovery of alcohols, chlorinated hydrocarbons, hydrocarbons and aromatics. Selexsorb CDX is specially formulated by Alcoa Industrial Chemicals for adsorption of polar organic compounds including sulfur-based molecules (mercaptans, sulfides, disulfides, thiophenes), nitrogen-based molecules (nitriles, amines, pyridines) and oxygenated hydrocarbon molecules (alcohol, glycols, aldehydes, ketons, ethers, peroxides). More benzene than thiophene was adsorbed on both activated carbon and modified activated alumina at pressures below  $1 \times 10^{-2}$  atm. This is surprising because Selexsorb was thought to adsorb thiophene more selectively than benzene. This result indicates that polarizability may play a more important role (than permanent dipole moment and magnetic susceptibility) in adsorption on these two sorbents. At pressures higher than  $1 \times 10^{-2}$  atm, pore filling dominated hence benzene adsorbed less than thiophene because of the larger molar volume of benzene than thiophene.

**Comparison of thiophene adsorption on all sorbents.** Thiophene adsorption isotherms on all sorbents are compared in Figure 13. It is clearly seen that Ag-Y and Cu-Y could adsorb significantly larger amounts of thiophene even at very low pressures.

#### **Purification capability**

For purification, as has been shown for the removal of ppm levels of dienes from olefins, an important consideration is the separation factor; and the separation factor should be evaluated at *low* concentrations of the solute but at *high* concentrations of the solvent. In other words, the capacity for the dilute solute (at ppm level) is a factor that determines the purification. As stated above, the separation factor ( $\alpha$ ) is given by:

$$\alpha_{12} = X_1 Y_2 / (X_2 Y_1) \quad (2)$$

where X and Y are mole fractions in the adsorbed and fluid phases, respectively. In our

case, component 1 is thiophene and component 2 is benzene. A further important parameter is the capacity of the sorbent for the solute at low concentrations. Hence, the ability of the sorbent for purification depends on the amount of thiophene adsorbed at the ppm levels.

To estimate the adsorption amount in the mixture of thiophene and benzene, the pure-component adsorption data were first fitted by both D-A (Dubinin-Astakhov) and L-F (Langmuir-Freundlich) isotherms. The separation factors of thiophene over benzene were then obtained using the equivalent multi-component isotherms, as described previously. The conversion of molar adsorbed amount to volumetric adsorbed amount and *vice versa* were performed in the same way as Doong and Yang. The molar volumes of thiophene in this work were 79.7 cc/mol at 90 °C, 83.0 cc/mol at 120°C and 89.8 cc/mol at 180°C, and those of benzene were 90.5 cc/mol at 90°C, 94.6 cc/mol at 120°C and 102.9 cc/mol at 180°C. The adsorbed molar volumes were assumed to be the same in both single- and mixed-gas adsorption. Separation factors were calculated for two cases:  $1 \times 10^{-4}$  atm thiophene/1 atm benzene and  $1 \times 10^{-5}$  atm thiophene/1 atm benzene.

The parameters for the D-A and L-F equations are given in Table 8 and the resulting separation factors are listed in Table 9. Some of the D-A parameters were not applicable for the Doong/Yang model for mixtures, when the volumetric adsorbed amount of benzene was much higher than that of thiophene. The separation factors of thiophene over benzene follow the order: Ag-Y > Na-ZSM-5 > Cu-Y  $\cong$  activated carbon >> Na-Y >> H-USY  $\cong$  modified activated alumina. This order can be explained as follows. As described earlier, the ability of the sorbent for purification depends on the amount of thiophene adsorbed at the ppm levels, compared with the amount of benzene adsorbed at high concentration. Ag-Y and Na-ZSM-5 showed fairly flat isotherms of thiophene over the entire partial pressure range, resulting in the higher separation factors. In fact, Ag-Y and Na-ZSM-5 maintained 65% and 47% of thiophene adsorption amounts at  $2.3 \times 10^{-5}$  atm compared with those at  $1.3 \times 10^{-2}$  atm, respectively. The advantage of Ag-Y against Na-ZSM-5 was further enhanced by the fact that Ag-Y was slightly selective for thiophene than benzene, while thiophene/benzene isotherms on Na-ZSM-5 were virtually the same. On the other hand, Cu-Y and activated carbon could adsorb a certain

amount of thiophene/benzene, but smaller adsorption amounts at lower pressures reduced the separation factors considerably. Only 18% and 5% of thiophene adsorption amounts were retained by Cu-Y and activated carbon between  $2.5 \times 10^{-5}$  atm and  $1.3 \times 10^{-2}$  atm, respectively. Larger adsorption amounts of benzene than thiophene by Selexsorb CDX made the separation factor of this sorbent extremely low.

Another important parameter for purification is the sorbent capacity for the solute at very low concentrations, i.e., for thiophene at ppm levels. The sorbent capacities are shown in Figure 13. At  $2.3 \times 10^{-5}$  atm, the capacities for thiophene follow the order: Ag-Y & Cu-Y >> Na-ZSM-5 > activated carbon > Na-Y > modified alumina & H-USY. Based on these two key parameters, the  $\pi$ -complexation sorbents are clearly the best.

### Heat of adsorption

Heats of adsorption were calculated using the Clausius-Clapeyron equation from isotherms at two different temperatures, and are shown in Table 10. All the heats of thiophene/benzene adsorption had the tendency to decrease as the loading increased. This is a common phenomenon for the sorbents such as ion-exchanged zeolites that have heterogeneous sites. The heats of adsorption on activated carbon, in particular, ranged widely from 23.9 kcal/mol (at 0.5 mmol/g loading) to 8.0 kcal/mol (at 3 mmol/g). Ag-Y and Cu-Y exhibited the higher heats of adsorption than Na-Y for both benzene and thiophene; it is believed due to  $\pi$ -complexation. More importantly, the heats of adsorption for thiophene were higher than that of benzene. These experimental results can be explained by molecular orbital calculation and NBO analysis, which will be discussed shortly.

At the low loading of 0.5 mmol/g, Na-ZSM-5 showed nearly the same heats of adsorption as Na-Y for both thiophene and benzene. The different pore dimensions (5.2-5.6 Å for ZSM-5 vs. 7.4 Å for Na-Y) apparently had no influence on the heats of adsorption. It is not clear why the amounts adsorbed on Na-Y decreased sharply at very low pressures while that on Na-ZSM-5 maintained.

### Bond Energies, Geometries and NBO results

The energies of adsorption calculated using equation 1 for thiophene and benzene are summarized in Table 11. The theoretical calculations indicate that the  $\pi$ -



complexation strengths follow the order  $\text{CuZ} > \text{AgZ}$  and more importantly, thiophene  $>$  benzene. This trend is in agreement with the experimental data, in Table 10. In fact, the molecular orbital results on CuZ and AgZ are in excellent agreement with the experimental data. Both chloride and zeolite models were used as the anion in the theoretical calculations, while only zeolite framework was the anion in the experiment. It is believed that the anion has a large effect on the  $\pi$ -complexation bonds. The bond energies on the zeolites (Z) are significantly higher than that on the chlorides (Table 11). This result indicates that the zeolite anion is more electronegative than the chloride anion, which has been revealed by Chen and Yang in their *ab initio* molecular orbital calculations. In the optimized structures of thiophene-MCl complexes, the distance between the thiophene molecule and Cu ion is about 0.3 Å shorter than that of thiophene and Ag ion for chloride. The NBO analysis is summarized in Tables 12 and 13. There is some donation of electron charges from the  $\pi$ -orbital of thiophene to the vacant s orbital of metals known as  $\sigma$  donation and, simultaneously, back donation of electron charges from the d orbitals of metals to  $\pi^*$  orbital (i.e., anti-bonding  $\pi$  orbital) of thiophene or  $\pi$  back-donation. It appears that the  $\sigma$  donation is more predominant for thiophene and the  $\pi$  back-donation is more important for benzene. Comparing the two anions, zeolite anion and chloride anion, the NBO results show that both  $\sigma$  donation and d -  $\pi^*$  backdonation are significantly stronger with the zeolite anion bonded to  $\text{Ag}^+$  or  $\text{Cu}^+$ . The charge transfer results again confirmed the experimental data that the relative strengths of the  $\pi$ -complexation bonds follow the order: thiophene  $>$  benzene and  $\text{Cu}^+ > \text{Ag}^+$ .

### **Uptake Rates**

Table 14 compares diffusion time constants for Ag-Y, Cu-Y and Na-Y. These constants were calculated from the uptake rates using the solution for Fick's law. Uptake rates among the three sorbents were very similar and no notable differences between thiophene and benzene were observed. These rates are reasonably fast for practical applications.

In this experiment, vapor-phase benzene/thiophene adsorption isotherms were investigated to develop new sorbents for desulfurization. Among the sorbents studied, it was found that Cu-Y and Ag-Y exhibited excellent adsorption performance (capacities and separation factors) for desulfurization. This enhanced performance

compared to Na-Y is believed to be due to the  $\pi$ -complexation with  $\text{Cu}^+$  and  $\text{Ag}^+$ . Molecular orbital calculations confirmed the relative strengths of  $\pi$ -complexation: thiophene > benzene and  $\text{Cu}^+ > \text{Ag}^+$ . In an actual desulfurization process, liquid phase adsorptions such as batch adsorption or fixed-bed adsorption column around room temperatures are viable options. Liquid phase experiments are described herein. Even in the case of liquid phase separation, enhanced selectivities based on  $\pi$ -complexation studied in this experiment are applicable.

Table 7. Thiophene Adsorption Amount Normalized by Cation Content.

(thiophene/cation molar ratio)

| Adsorbent                       | Ag-Y          | Cu-Y          |
|---------------------------------|---------------|---------------|
| Cations for $\pi$ -complexation | $\text{Ag}^+$ | $\text{Cu}^+$ |
| Cation Content in Zeolite (wt%) | 38.2          | 8.29          |
| Amount Adsorbed (molar ratio)   | 0.42          | 0.92          |

Table 8 Parameters for the D-A and L-F Equations.

|               |          |        | L-F Equation   |         |      | D-A Equation   |                |        |      |                |
|---------------|----------|--------|----------------|---------|------|----------------|----------------|--------|------|----------------|
|               |          |        | q <sub>0</sub> | B       | n    | q <sub>0</sub> | V <sub>0</sub> | C      | n    | P <sub>s</sub> |
|               |          |        | (mmol/g)       | (1/atm) | (-)  | (mmol/g)       | (cc/g)         | (-)    | (-)  | (atm)          |
| Ag-Y          | Benzene  | 120 °C | 3.133          | 3.40    | 7.67 | 2.416          | 0.2286         | 0.0559 | 1.56 | 2.96           |
|               |          | 180 °C | 2.032          | 155.5   | 1.85 | 2.008          | 0.2066         | 0.0786 | 4.57 | 10.07          |
|               | Thiophen | 120 °C | 3.200          | 4.416   | 6.59 | 2.986          | 0.248          | 0.0609 | 1.12 | 2.68           |
|               |          | 180 °C | 2.602          | 6.13    | 4.77 | 2.329          | 0.2091         | 0.0699 | 1.87 | 9.42           |
| Cu-Y          | Benzene  | 90 °C  | 2.989          | 292.6   | 1.76 | 2.940          | 0.266          | 0.0889 | 4.36 | 1.34           |
|               |          | 120 °C | 2.897          | 178.6   | 1.59 | 2.929          | 0.2771         | 0.1008 | 3.95 | 2.96           |
|               | Thiophen | 90 °C  | 3.910          | 196.4   | 1.80 | 3.826          | 0.3048         | 0.0935 | 3.99 | 1.19           |
|               |          | 120 °C | 3.548          | 121.5   | 1.65 | 3.548          | 0.2946         | 0.1010 | 3.81 | 2.68           |
| Na-Y          | Benzene  | 120 °C | 2.781          | 13985   | 0.89 | 2.789          | 0.2639         | 0.0980 | 6.80 | 2.96           |
|               |          | 180 °C | 2.820          | 449.0   | 0.90 | 2.872          | 0.2956         | 0.1200 | 4.73 | 10.07          |
|               | Thiophen | 120 °C | 2.681          | 13548   | 0.84 | 2.658          | 0.2207         | 0.1050 | 7.30 | 2.68           |
|               |          | 180 °C | 2.739          | 15001   | 0.50 | 2.846          | 0.2555         | 0.1330 | 7.54 | 9.42           |
| PCB-AC        | Benzene  | 90 °C  | 7.828          | 4.47    | 2.46 | 6.329          | 0.5725         | 0.1638 | 1.71 | 1.34           |
|               |          | 120 °C | 6.312          | 4.254   | 2.16 | 6.197          | 0.5863         | 0.1847 | 1.62 | 2.96           |
|               | Thiophen | 90 °C  | 7.231          | 5.54    | 2.29 | 8.936          | 0.7118         | 0.2246 | 1.24 | 1.19           |
|               |          | 120 °C | 6.996          | 6.39    | 1.66 | 7.236          | 0.6009         | 0.2193 | 1.59 | 2.68           |
| Na-ZSM5       | Benzene  | 90 °C  | 0.928          | 17.15   | 3.43 | 0.987          | 0.0893         | 0.0810 | 1.44 | 1.34           |
|               |          | 120 °C | 0.795          | 14.66   | 3.47 | 0.826          | 0.0781         | 0.0793 | 1.64 | 2.96           |
|               | Thiophen | 90 °C  | 1.023          | 16.91   | 3.27 | 1.036          | 0.0825         | 0.0880 | 1.79 | 1.19           |
|               |          | 120 °C | 0.811          | 16.36   | 3.30 | 0.856          | 0.0711         | 0.0832 | 1.70 | 2.68           |
| Selexsorb CDX | Benzene  | 90 °C  | 1.182          | 1196.6  | 1.39 | 1.176          | 0.1064         | 0.0914 | 5.23 | 1.34           |
|               |          | 120 °C | 1.096          | 75902   | 0.71 | 1.109          | 0.1049         | 0.1049 | 8.14 | 2.96           |
|               | Thiophen | 90 °C  | 1.223          | 29720   | 0.79 | 1.239          | 0.0987         | 0.1141 | 6.78 | 1.19           |
|               |          | 120 °C | 1.134          | 133016  | 0.55 | 1.158          | 0.0962         | 0.1265 | 8.20 | 2.68           |
| H-USY         | Benzene  | 90 °C  | 4.258          | 568.1   | 0.48 | 4.359          | 0.3943         | 0.2800 | 4.21 | 1.34           |
|               |          | 120 °C | 3.895          | 63.573  | 0.53 | 4.100          | 0.3879         | 0.2825 | 3.63 | 2.96           |
|               | Thiophen | 90 °C  | 4.568          | 382.1   | 0.51 | 4.689          | 0.3735         | 0.2939 | 3.55 | 1.19           |
|               |          | 120 °C | 4.356          | 24.41   | 0.61 | 4.599          | 0.3819         | 0.2820 | 4.07 | 2.68           |

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Table Separation Factors estimated by the D-A and L-F Equations at 120 °C.

| Thiophene(atm)/Benzene(atm) | LF Equation |         | DA Equation |        |
|-----------------------------|-------------|---------|-------------|--------|
|                             | 1E-4/1      | 1E-5/1  | 1E-4/1      | 1E-5/1 |
| Ag-Y                        | 3300        | 23000   | 1600        | 11000  |
| Cu-Y                        | 31          | 78      | 360         | 700    |
| Na-Y                        | 0.16        | 0.10    | *** 1)      | *** 1) |
| PCB-AC                      | 64          | 160     | 33          | 83     |
| Na-ZSM5                     | 700         | 3500    | *** 1)      | *** 1) |
| Selexsorb CDX               | 9.6E-04     | 1.5E-04 | *** 1)      | *** 1) |
| H-USY                       | 1.2E-03     | 2.7E-04 | *** 1)      | *** 1) |

1) Not applicable to Doong/Yang extension.

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Table. Heat of adsorption (kcal/mol) calculated from isotherms at different temperatures.

|           | Na-Y                   | Ag-Y                   | Cu-Y                   | H-USY                 | Na-ZSM5                  | Activated Carbon       | Activated Alumina      |
|-----------|------------------------|------------------------|------------------------|-----------------------|--------------------------|------------------------|------------------------|
|           | (Si/Al=2.43)           | (Si/Al=2.43)           | (Si/Al=2.43)           | (Si/Al=195)           | (Si/Al=10)               | Type PCB               | Selexsorb CDX          |
| Thiophene | 19.1-19.6<br>(0.5-2.0) | 21.3-21.5<br>(1.5-1.7) | 20.8-22.4<br>(2.0-3.0) | 7.9-11.2<br>(0.1-0.3) | 18.6-19.2<br>(0.45-0.60) | 8.0-23.9<br>(0.5-3.0)  | 16.1-17.5<br>(0.2-1.0) |
| Benzene   | 17.0-18.2<br>(1.5-2.0) | 19.0-20.1<br>(1.5-1.8) | 19.3-21.8<br>(1.8-2.5) | 6.6-13.1<br>(0.1-0.5) | 16.5-17.9<br>(0.45-0.65) | 13.1-16.1<br>(1.0-3.0) | 16.8-19.6<br>(0.6-1.0) |

\*) Numbers in parentheses indicate the adsorption amounts (mmol/g) for calculation.

\*\*) The heats of adsorption decreased with loading in all cases.

Table 11. Summary of energies of adsorption for thiophene and benzene in kcal/mol calculated from molecular orbital theory (Z denotes Zeolite anion)

|      | $E_{\text{ads}}(\text{Thiophene})$ | $E_{\text{ads}}(\text{Benzene})$ |
|------|------------------------------------|----------------------------------|
| CuCl | 13.5                               | 12.4                             |
| AgCl | 9.0                                | 8.6                              |
| CuZ  | 21.4                               | 20.5                             |
| AgZ  | 20.0                               | 19.1                             |

Table 12. Summary of NBO analysis\* of  $\pi$ -complexation between thiophene and MCl/MZ

| MX   | C $\rightarrow$ M interaction<br>( $\sigma$ donation)<br>$q_1$ | M $\rightarrow$ C interaction<br>(d - $\pi^*$ backdonation)<br>$q_2$ | Net Change<br>$q_1 + q_2$ |
|------|--|--|---------------------------|
| CuCl | 0.037  | -0.022   | 0.015                     |
| AgCl | 0.022  | -0.014   | 0.008                     |
| CuZ  | 0.112  | -0.063   | 0.049                     |
| AgZ  | 0.101  | -0.086   | 0.015                     |

\*  $q_1$  is the amount of electron population change in valence s orbitals of the metal, and  $q_2$  is the total amount of electron population decrease in valence d orbitals of the metal.

Table 13. Summary of NBO analysis\* of  $\pi$ -complexation between benzene and MCl/MZ

| MX   | C $\rightarrow$ M interaction<br>( $\sigma$ donation)<br>$q_1$ | M $\rightarrow$ C interaction<br>(d - $\pi^*$ backdonation)<br>$q_2$ | Net Change<br>$q_1 + q_2$ |
|------|--|--|---------------------------|
| CuCl | 0.011  | -0.013   | -0.002                    |
| AgCl | 0.003  | -0.007   | -0.004                    |
| CuX  | 0.078  | -0.119   | -0.041                    |
| AgX  | 0.043  | -0.045   | -0.002                    |

\*  $q_1$  is the amount of electron population change in valence s orbitals of the metal, and  $q_2$  is the total amount of electron population decrease in valence d orbitals of the metal.

Table 14 Diffusion Time Constants (1/s) of Thiophene and Benzene

|      | Thiophene                |                           | Benzene                  |                           |
|------|--------------------------|---------------------------|--------------------------|---------------------------|
|      | Pressure Change<br>(atm) | D/r <sup>2</sup><br>(1/s) | Pressure Change<br>(atm) | D/r <sup>2</sup><br>(1/s) |
| Ag-Y | 1.9E-5 - 1.6E-4          | 2.0E-05                   | 5.7E-5 - 5.5E-4          | 5.4E-05                   |
|      | 5.6E-4 - 1.8E-3          | 3.3E-04                   | 5.5E-4 - 5.4E-3          | 1.8E-04                   |
|      | 1.8E-3 - 1.5E-2          | 1.2E-04                   | 5.4E-3 - 2.6E-2          | 4.2E-04                   |
| Cu-Y | 2.3E-5 - 8.8E-5          | 1.3E-05                   | 3.2E-5 - 1.2E-4          | 2.0E-05                   |
|      | 8.8E-5 - 4.0E-4          | 2.3E-05                   | 1.2E-4 - 5.4E-4          | 5.2E-05                   |
|      | 4.0E-4 - 2.2E-3          | 1.5E-04                   | 5.4E-4 - 3.0E-3          | 3.3E-04                   |
|      | 2.2E-3 - 1.3E-2          | 1.4E-04                   | 3.0E-3 - 1.8E-2          | 3.7E-04                   |
| Na-Y | 8.8E-5 - 4.0E-4          | 1.7E-05                   | 0 - 1.5E-4               | 1.5E-05                   |
|      | 4.0E-4 - 2.2E-3          | 1.6E-04                   | 1.5E-4 - 5.5E-4          | 2.6E-05                   |
|      | 2.2E-3 - 1.3E-2          | 2.8E-04                   | 5.5E-4 - 5.4E-3          | 5.6E-04                   |
|      | 1.3E-2 - 2.9E-2          | 5.4E-04                   | 5.4E-3 - 2.6E-2          | 2.4E-04                   |

As mentioned hereinabove, it has further been fortuitously found that the sorbents of the present invention also are excellent sorbents for removal of aromatics. A detailed description of removal of aromatics follows.



Adsorption of benzene and cyclohexane on various Y-zeolites was investigated in order to develop sorbents for the purification of aliphatics by removal of aromatics. Ag-Y showed superior benzene/cyclohexane selectivities than Na-Y, Pd-Y and H-USY. Separation factors greater than  $10^5$  were obtained with Ag-Y at low concentrations of benzene. The high selectivities were achieved by the strong interaction between benzene and Ag-Y, while the interaction with cyclohexane was not influenced by the cations. Molecular orbital calculation revealed that benzene formed classical  $\pi$ -complexation bond with Ag-Y: donation of electron charges from the p-orbitals of benzene to the vacant s-orbital of the silver ( $\sigma$  donation) and, simultaneously, back donation of electron charges from d-orbitals of silver to  $\pi^*$  orbital of benzene ( $d-\pi^*$  back donation). Grand canonical Monte Carlo simulations were also performed for the adsorption isotherms. Potential parameters of benzene on Ag-Y including  $\pi$ -complexation were first developed. GCMC simulation and experiments were in excellent agreement for adsorption of benzene on Y-zeolites.

Purification of aliphatics by removing aromatics is important in both petrochemical industry and for pollution control. Because benzene (and aromatics) is known to be highly carcinogenic, concentration of benzene needs to be minimized in the automotive fuel. A number of separation processes have been employed to reduce the benzene concentration in a refinery's gasoline pool, so that it meets new reformulated gasoline requirements. In a typical benzene reduction process, a combination of extraction and distillation is used (Jeanneret, 1997). Also, removal of aromatics from kerosene improves the clean burning properties of the fuel and separation of the aromatics from the isoparaffins and naphthenes in lubricating oils improves the viscosity-temperature relationship (Bailes, 1983).

Because of the importance of aromatics/aliphatics separation and the problems associated with current separation processes, possible alternatives have been under continuing investigation. These include pervaporation (Hao et al, 1997), liquid membranes (Li, 1968), and the use of liquid inclusion complexes (Atwood, 1984). Purification of dilute aromatics from aliphatics (e.g., toluene and/or xylene in heptane) by temperature swing adsorption (TSA) was studied in the liquid phase (Matz and Knaebel, 1990). Commercially available sorbents were used: silica gel, activated alumina, activated carbon, zeolite 13X, and polymeric resin (XAD-7). Among

these sorbents, silica gel was considered the best due to its superior thermal-exchange capacity. However, the selectivities were low.

Adsorption is playing an increasingly important role in separations. However, its utility is limited by the availability of selective sorbents. The conventional sorbents and separations using them are based on van der Waals and electrostatic interactions between the sorbate and the sorbent. Studies of new sorbents using weak chemical bonds such as chemical complexation have begun only recently in our laboratory. As suggested by King (King, 1987), chemical complexation bonds are generally stronger than van der Waals interactions, yet weak enough to be reversible. Therefore, tremendous opportunities exist for developing new sorbents and new applications in separations by using weak chemical bonds, including various forms of complexation bonds.

The  $\pi$ -complexation is a sub-class of chemical complexation. It pertains to the main group (or d-block) transition metals, i.e., from Sc to Cu, Y to Ag, and La to Au in the periodic table (Cotton and Wilkinson, 1966). These metals or their ions can form the normal  $\sigma$ -bond to carbon and, in addition, the unique characteristics of the d orbitals in these metals or ions can form bonds with unsaturated hydrocarbons in a nonclassical manner. This type of bonding is broadly referred to as  $\pi$ -complexation. This  $\pi$ -complexation has been seriously considered for olefin/paraffin separations using liquid solutions containing silver or cuprous ions (Quinn, 1971; Ho et al., 1988; Keller et al., 1992; Blytas, 1992; Eldridge, 1993; Safarik and Eldridge, 1988). These involved gas-liquid operations. While gas-solid operation can be simpler as well as more efficient, particularly by pressure swing adsorption, the list of attempts for developing solid  $\pi$ -complexation sorbent is a short one.

More recently, several new sorbents based on  $\pi$ -complexation were prepared for selective olefin adsorption. These included  $\text{Ag}^+$ -exchanged resins (Yang and Kikkinides, 1995; Wu et al., 1997), monolayer CuCl on pillared clays (Cheng and Yang, 1995) and monolayer  $\text{AgNO}_3/\text{SiO}_2$  (Padin and Yang, 1997; Rege et al., 1998; Padin and Yang, 2000). Moreover, Ag ion-exchanged Y-Zeolite was developed to purify butene by removing trace amounts of butadiene (Padin et al., 1999). The purification performance of this sorbent was superior to that of NaY owing to  $\pi$ -complexation.

It is possible, in principle, to purify aromatics from aliphatics based on  $\pi$ -complexation. In the benzene molecules, the carbon atom is  $sp^2$  hybridized. Hence, each carbon has three  $sp^2$  orbitals and another  $P_z$  orbital. The six  $P_z$  orbitals in the benzene ring form the conjugative  $\pi$  bonds. The  $P_z$  orbitals also form the antibonding  $\pi^*$  orbitals, which are not occupied. When benzene interacts with transition metals, the  $\pi$ -orbitals of benzene could overlap with the empty or unfilled outer-shell  $s$  orbital of the transition metal to form a  $\sigma$ -bond. Furthermore, the vacant antibonding  $\pi^*$ -orbitals of benzene could overlap with the  $d$ -orbitals in the transition metals, similar to that formed in the olefin- $Cu^+$  bond (Huang et al, 1999a). In this work,  $Ag^+$  and  $Pd^{2+}$  ion-exchanged zeolites were selected for the study of aromatics/aliphatics separations, since these two cations have the most promising  $\pi$ -complexation capabilities, and they are stable. In order to understand the effects of  $\pi$ -complexation,  $Ag^+$  and  $Pd^{2+}$  ion-exchanged zeolites were compared with that of  $Na^+$  ion-exchanged zeolite and a high- $SiO_2$  zeolite.

Benzene and cyclohexane are an ideal pair of model compounds for studying selective sorbents for purification. These molecules have similar shapes, polarizabilities and volatilities (the boiling points are 80 °C for benzene and 81 °C for cyclohexane). The kinetic diameter of benzene, which is calculated from the minimum equilibrium cross-sectional diameter, is estimated to be 5.85 angstrom compared with 6.0 angstrom for cyclohexane (Breck, 1974). Therefore, benzene and cyclohexane were used in this work.

In addition to the experimental investigation, molecular orbital calculations were performed to obtain a basic understanding of the origin of the strong interactions of  $Ag$  ion-exchanged zeolite with benzene. Moreover, grand canonical Monte Carlo (GCMC) simulations were used to simulate/predict the isotherms. Many GCMC studies have been performed for predicting adsorption isotherms in zeolites. These include  $N_2$ ,  $O_2$ ,  $Ar$ ,  $Xe$ ,  $CH_4$ ,  $C_2H_4$  and  $C_4H_{10}$  on zeolite-A, X, Y and MFI-type Zeolite (Woods and Rowlinson, 1989; Razmus and Hall, 1991; Kravias and Myers, 1991; Watanabe et al., 1995). Adsorption of benzene on NaY, Heulandite and MFI-type zeolites has also been studied (Snurr et al., 1994; Kitagawa et al., 1996; Klemm et al., 1998; Laboy et al., 1999). However, these studies did not involve the effects of  $\pi$ -complexation on adsorption. In this study, benzene adsorption isotherms on  $Ag$  ion-exchanged Y-zeolite were simulated.

## Experimental Details

### *Sorbent Preparation*

The sorbents in this work were ion-exchanged zeolites. From earlier results on olefin/paraffin separations (Yang and Kikkinides, 1995; Wu et al., 1997; Cheng and Yang, 1995; Padin and Yang, 1997; Rege et al., 1998; Padin and Yang, 2000),  $\text{Ag}^+$  and  $\text{Pd}^{2+}$  were the most promising ions because of their strong  $\pi$ -complexation abilities.

Ion-exchange of zeolites was accomplished with aqueous solutions. Faujasite was selected as the zeolite framework structure for ion-exchange, because of its large pore aperture (7.4 angstrom), large pore volume (0.489 ml/ml) and wide range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios (1- $\infty$ ). Two as-received zeolites, Na-type Y-Zeolite (Na-Y, Si/Al=2.43, Strem Chemical) and H-type ultra-stable Y-Zeolite (H-USY, Si/Al=195, TOSOH CORPORATION, HSZ-390HUA), were used in this study.  $\text{Pd}^{2+}$  type Y-Zeolite was prepared by exchanging Na-Y zeolite with  $\text{Pd}(\text{NO}_3)_2$  (Aldrich) in an aqueous solution (Li et al., 1994). First, Na-Y was exchanged using 2-fold excess of  $\text{Pd}(\text{NO}_3)_2$  (0.005M) at 80 °C for 24h. After the exchange, the zeolite suspension was filtered and washed with copious amount of deionized water. The product was dried at 110 °C overnight in air.  $\text{Ag}^+$  ion-exchange was prepared at room temperature for 24 h in the same manner as  $\text{Pd}^{2+}$  exchange, using 2-fold excess  $\text{AgNO}_3$  (0.1M).

### *Adsorption Isotherms and Uptake Rates*

Single component isotherms for benzene and cyclohexane were measured using standard gravimetric methods. A Shimadzu TGA-50 automatic recording microbalance was employed. Helium (Pre-purified grade, Metro Welding, 99.995%) was used as the carrier gas and was first passed through two consecutive gas-wash bottles (to ensure saturation) which contained benzene (HPLC grade, Sigma-Aldrich, 99.9+%) or cyclohexane (HPLC grade, Aldrich, 99.9+%). After diluting the concentration to the desired value by blending with additional helium (total flowrate: 250 cc/min), the mixture was directed into the microbalance.

Isosteric heats of adsorption were calculated using the Clausius-Clapeyron equation from isotherms at different temperatures. Nitrogen isotherms at 77K measured with a Micromeritics ASAP 2010 system were used for pore size distribution and pore volume determination. Pore size distributions were calculated with Horvath-Kawazoe equation (Horvath and Kawazoe, 1983; Cheng and Yang, 1994). Pore volumes were calculated at 0.95 P/Po. The

overall diffusion time constants,  $D/r^2$ , were calculated from the uptake rates (Yeh, 1989). In this work, the short time region was used.

### **Molecular Orbital Calculation Details**

The  $\pi$ -complexation bonding between olefins and sorbents have been extensively investigated using molecular orbital (MO) calculations (Chen and Yang, 1996; Huang et al., 1999a, 1999b). More recently, MO studies were extended to benzene adsorption on various salts such as CuCl and AgCl (Takahashi et al.). In this work, similar MO studies for benzene adsorption on Ag ion-exchanged zeolite were performed using a cluster model of Ag-zeolite. The Gaussian 94 Program (Frisch et al., 1995) in Cerius2 molecular modeling software (Bowie, 1995) from Molecular Simulation, Inc. was used for calculations. MO calculations for benzene and Ag zeolite were performed at the Hartree-Fock (HF) and density functional theory (DFT) level. The 3-21G basis set is the split-valence basis set, which has been used successfully for many simulations for benzene adsorption on zeolites (O'Malley and Braithwaite, 1995), protonation reaction of propylene and isobutene on zeolite (Viruera-Martin et al., 1993) and O<sub>2</sub>, N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> adsorption on Ag-Zeolites (Chen and Yang, 1996). The reliability of this basis set has been confirmed by the accuracy of calculation results in comparison with experimental data. Therefore, the 3-21G basis set was employed for both geometry optimization and natural bond orbital (NBO) analysis.

### ***Geometry Optimization and Energy of Adsorption Calculations***

The restricted Hartree-Fock (RHF) theory at the 3-21G level basis set was used to determine the geometries and the bonding energies of benzene on Ag zeolite cluster, since Ag<sup>+</sup> has filled d-orbitals with spin = 1.

The computational model used for Ag zeolite were the same as that used by Chen and Yang (Chen and Yang, 1996), since this model yielded heats of adsorption of N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> on Ag zeolite that agreed well with experimental data. The simplest cluster model, (HO)<sub>3</sub>Si-O(Ag)-Al(OH)<sub>3</sub>, was chosen for this work. The optimized structures were then used for bond energy calculations according to the following expression:

$$E_{\text{ads}} = E_{\text{adsorbate}} + E_{\text{adsorbent}} - E_{\text{adsorbent-adsorbate}} \quad (1)$$

Where  $E_{\text{adsorbate}}$  is the total energy of benzene,  $E_{\text{adsorbent}}$  is the total energy of the bare adsorbent i.e., the Ag zeolite cluster, and  $E_{\text{adsorbent-adsorbate}}$  is the total energy of the adsorbate/adsorbent system.

### ***Natural Bond Orbital (NBO) Analysis***

The optimized structures were also used for NBO analysis at the B3LYP/3-21G level. The B3LYP (Becke, 1993a) approach is one of the most useful self-consistent hybrid (SCH) approaches (Becke, 1993b), which is Becke's 3-parameter nonlocal exchange functional (Becke, 1992) with the nonlocal correlation functional of Lee, Yang and Parr (Lee et al., 1988).

The NBO analysis performs population analysis pertaining to the localized wave-function properties. It gives a better description of the electron distribution in compounds of high ionic character, such as those containing metal atoms (Reed et al., 1985). It is known to be sensitive for calculating localized weak interactions, such as charge transfer, hydrogen bonding and weak chemisorption. Therefore, the NBO program (Glendening et al., 1995) was used for studying the electron density distribution of the adsorption system.

### **Monte Carlo Simulation Details**

Grand canonical ensemble (at a fixed pressure) Monte Carlo simulation was performed utilizing the Cerius2 molecular modeling software (Bowie, 1995) on a Silicon Graphics Indigo2 workstation running IRIX v.6.5. After the "crystal builder" module was used to set up the zeolite models, energy expressions and parameters for force field were input by the "force field editor" module. The "sorption" module was then used for benzene adsorption simulations.

The simulation was performed at 120 °C and 180 °C for at least 1,000,000 configurations. During the simulation, the sorbate molecules interacted with the potential field generated by sorbate-sorbent and sorbate-sorbate interactions. The initial configurations contained no sorbate molecules. Each subsequent configuration was generated by one of four moves: CREATE, DESTROY, TRANSLATE and ROTATE. Molecular creation attempts were made at random points within the accessible portion of the zeolite lattice with the criterion that there be no overlapping sites (i.e. creations which results in interaction sites which were closer than half the sum of the van der Waal's radii of the two sites were rejected). Translation and rotation were performed with the same rejection criterion. For non-overlapping sites, the change in the potential energy accompanying the new configuration was calculated and subsequently accepted or rejected in accordance with standard acceptance probabilities (Molecular Simulation Inc., 1998).

### ***Zeolite Models***

The structure determined from powder neutron diffraction data by Fitch et al. (Fitch et al., 1986) was used as the structure for Na-Y Zeolite (Si/Al=2.43). The location of the Na cations were 32 atoms on SII sites, 16 atoms on SI sites and 8 atoms on SI' sites. Na cations on SI and SI' sites were located in such a manner that two adjacent SI and SI' were not simultaneously occupied. This is due to the electrostatic repulsion caused by their small separation of 0.218 nm (Fitch et al., 1986). The position of Al in the framework was randomly chosen using the "disorder" function in the "crystal builder" module that obeyed the Loewenstein rule. No charge-free "blocking atom" was added because large molecules such as benzene were not located in the site, which was actually sterically inaccessible.

For the simulation of Ag ion-exchanged zeolite (Si/Al=2.43), the Na cations in Na-Y were replaced by Ag maintaining the same cation locations. An all silica Y-Zeolite structure was used to simulate Ultra-Stable Y-Zeolite (Si/Al=195) since this zeolite has less than one Al atom per unit cell.

Until recently, the location of the Ag cation was not accurately determined. Using neutron diffraction data, Hutson et al (Hutson et al., 2000) reported the Ag location and occupancies of Ag in Ag-Y (Si/Al=2.43) after 450 °C dehydration. Their results showed that the Ag cation sites were 28 atoms on SII sites, 4 atoms on SII' site, 11 atoms on SI sites and 12 atoms on SI' sites. Simultaneous occupancy of Ag cations at SII and SII' as well as SI and SI' sites was unlikely due to the large repulsion. This location is very similar to the location of Na cations in Na-Y reported by Fitch et al (1986). Therefore, the zeolite model for Ag-Y used in this work is considered to reflect the actual Ag cation locations in Ag-Y (Si/Al=2.43).

### ***Forcefield Determination***

One of the most important factors for GCMC simulation is the selection of an energy expression and parameters for the forcefield. The forcefield used in these simulations was a modified version of Cerius2 Sorption Demontis Forcefield, since Demontis et al. simulated the mobility of benzene in Na-Y zeolite successfully using molecular dynamics methods (Demontis et al., 1989). In this model, the total potential energy ( $U_{\text{Total}}$ ) between the zeolite lattice and adsorbate molecules is written as the sum of the interactions between adsorbate molecules(AA) and that between the adsorbate molecules and the zeolite lattice (AZ).

$$U_{Total} = U_{AA} + U_{AZ} \quad (2)$$

Interactions between adsorbate molecules ( $U_{AA}$ ) were described as the sum of the atom-atom Buckingham potentials (the first and second terms below), which have shown to yield reasonable predictions for liquid and solid benzene (Williams and Cox, 1984), and the Coulombic interaction potentials (the third term below).

$$U_{ij} = A_{ij} \exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6} + \left( \frac{q_i q_j}{r_{ij}} \right) \quad (3)$$

The first and second terms represent, respectively, the repulsive and dispersive potential energies between sites "i" and "j", and the third term represents the interaction potential between point charges  $q_i$  and  $q_j$  of sites "i" and "j" separated by a distance  $r_{ij}$ .

The interactions between the adsorbate molecules and the zeolite lattice ( $U_{AZ}$ ) is written as the sum of the atom-atom Lennard-Jones 12-6 potential and the Coulombic interaction potentials.

$$U_{ij} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \left( \frac{q_i q_j}{r_{ij}} \right) \quad (4)$$

Following the empirical approach used by Razman and Hall (Razmus and Hall, 1991), Watanabe et al. (Watanabe et al., 1995) used the empirical approach to parameterize the forcefield for adsorption of  $N_2$ ,  $O_2$ , and Ar in type A and faujasite zeolites. The dispersive part of the Lennard-Jones 12-6 potential ( $U_{dispersion}$ ) was written using an adjustable parameter ( $\beta_i$ ) of the adsorbate and the polarizabilities ( $\alpha$ ) of the atoms of the adsorbate molecules (i) and in the zeolite lattice (j).

$$U_{dispersion} = -\beta_i \left( \frac{\alpha_i \alpha_j}{r_{ij}^6} \right) \quad (5)$$

The potential energy well depth parameter,  $\epsilon_{ij}$ , is then written as

$$\epsilon_{ij} = \beta_i \left( \frac{\alpha_i \alpha_j}{4\sigma_{ij}^6} \right) \quad (6)$$

The Lennard-Jones parameter,  $\sigma_{ij}$ , for the adsorbate-zeolite interaction is given by the mixing rule,

$$\sigma_{ij} = \left( \frac{\sigma_i + \sigma_j}{2} \right) \quad (7)$$



The  $\sigma_j$  for the zeolite lattice are related to the van der Waals radii,  $R_j$ , of the respective ions by

$$R_j = 2^{1/6} \sigma_j \quad (8)$$

The well depth parameter,  $\varepsilon_{ij}$ , is assumed to be a geometric combination of  $\varepsilon_i$  and  $\varepsilon_j$ ,

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{0.5} \quad (9)$$

The van der Waals energy in the periodic framework was calculated using a minimum image convention with an interaction cut-off distance of 1 nm. The Coulombic term was evaluated using the Ewald summation method (Allen and Tildesley, 1987).

The potential parameters used for Na-Y, Ag-Y and H-USY are listed in Table 15. The potential parameters for Na-Y are the same as that of Demontis et al (Demontis et al., 1989). Van der Waals interactions between adsorbate and zeolite cage were modeled by means of interactions between the (C,H) and (Na,O) atoms. Interactions with the Si and Al atoms were neglected because they were well shielded by the oxygen atoms of the  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra. Electrostatic interactions between all charges were included in the potential energy calculation. As for Ag-Y and all silica Y zeolites, modification of parameters was performed using the mixing rule and the geometric combination rule. The detailed scheme for parameterization will be discussed shortly.

#### *Assignment of charges for adsorbate and adsorbent*

Assignment of charges also has a significant impact on simulation results when the Coulombic interactions are not negligible. In this work, the existing model for benzene in Cerius<sup>2</sup> was used. In this model, each carbon in benzene carries -0.093 point charge, while hydrogen carries +0.093. These values were nearly the average values from the various charge determination methods: MOPAC (0.1022), ZINDO (0.072) and charge equilibration method ( $Q_{eq}$ ) by Rappe and Goddard (0.1147) (Rappe and Goddard, 1991).

The point charges of zeolite were assigned either by (i) using the point charges in the literature or (ii) calculating by means of the charge equilibration method in the Cerius2 software. In this work, Na, Si/Al, O in Na-Y carried the charges of +0.78, +1.2125 and -0.72, respectively, since these values were successfully used in quantum mechanics simulations (Kitagawa et al., 1996). Here, no distinction was made between Si and Al atoms in terms of point charges. Charges of Ag-Y and all-silica Y-Zeolites were calculated by the charge equilibration method: Ag(+0.45), Si/Al(+1.16875), O(-0.65), which will be referred to as **Case I** for Ag-Y, and

Si(+1.2650), O(-0.6325) for H-USY. In order to investigate the effect of the assigned charges to the isotherm simulation results, the same charges that were used for Na-Y, i.e., Ag(+0.78), Si/Al(+1.2125) and O(-0.72), were also used for Ag-Y. This case is referred to as **Case II** for Ag-Y. For all cases, regardless of the positions of cations and framework atoms (Si, Al, O), the same values of point charge were assigned to the same atoms throughout the simulation unit cell, even though the point charge might vary with the position of the atom. The Ag cation charges used for Monte Carlo simulation were also consistent with the values calculated by molecular orbital method at MP2/3-21G (Ag charge : +0.49) or MP2/LanL2DZ level (Ag charge : +0.74) using the zeolite cluster model (Chen and Yang, 1996).

## Results and Discussion

### Experimental

#### *Benzene/cyclohexane adsorption isotherms*

Pure component isotherms of benzene and cyclohexane were measured for H-USY(Si/Al=195), Na-Y(Si/Al=2.43), Ag-Y(Si/Al=2.43), and Pd-Y(Si/Al=2.43) at 120 and 180 °C, shown in Figures 22-25. Isosteric heats of adsorption calculated using the Clausius-Clapeyron equation are listed in Table 16.

In the case of H-USY, the adsorbed amounts of cyclohexane were higher than that of benzene at > 0.04 atmosphere. This result qualitatively agreed with calculations using the Horvath-Kawazoe theory (Horvath and Kawazoe, 1983; Cheng and Yang, 1994). The threshold pore-filling vapor pressures of cyclohexane and benzene at 120 °C and 180 °C were calculated using the spherical pore model of the H-K method. The threshold pressure is the pressure where the steep rise in the isotherm occurs. At both temperatures, it was found that the pore-filling pressure of cyclohexane was 20 % lower than that of benzene. The reason for this difference was the larger polarizability ( $11.0 \times 10^{-24}$  cm<sup>3</sup> for cyclohexane and  $10.3 \times 10^{-24}$  cm<sup>3</sup> for benzene) and magnetic susceptibility ( $11.3 \times 10^{-29}$  cm<sup>3</sup> for cyclohexane and  $9.1 \times 10^{-29}$  cm<sup>3</sup> for benzene) of cyclohexane. However, the calculated isosteric heat of adsorption of benzene was slightly higher than that of cyclohexane. A possible reason for the larger heat of benzene adsorption was the existence of H<sup>+</sup> in the zeolite, although the number of proton was extremely small (less than one per unit cell). The interaction between protons in zeolite and  $\pi$ -electrons of benzene might be stronger than the interaction between oxygen in zeolite and benzene. Therefore, the amounts of

benzene adsorption were slightly larger than that of cyclohexane at less than 0.04 atm, leading to its higher heat of adsorption.

On all other sorbents investigated in this work, larger amounts of benzene were adsorbed at all pressure ranges. Heats of adsorption for benzene were 18 kcal/mol for Na-Y and 21 kcal/mol for Ag-Y, while heats of adsorption for cyclohexane were 10-12 kcal/mol for both Na-Y and Ag-Y. These results are clearly due to the strong interactions between the cations in zeolite and the benzene molecule. Consequently, Ag-Y and Na-Y could adsorb large amounts of benzene even at the pressure of less than 0.01 atm. The heats of adsorption on Na-Y were comparable to previous work (Barthomeuf and Ha, 1973). Most importantly, Ag-Y showed the strongest interactions for benzene and the largest heats of adsorption (20.5 kcal/mol). For cyclohexane adsorption, the adsorption amounts and heat of adsorption were almost the same between Ag-Y and Na-Y, since  $\pi$ -complexation was absent for cyclohexane. A detailed discussion will be made in the section of molecular orbital calculation and Monte Carlo simulation results. These results indicated that improved purification performance of benzene from cyclohexane is possible using Ag-Y. The isotherms of both Ag-Y and Na-Y are reversible, although it took a little longer time to desorb benzene and cyclohexane. For example, 200 minutes are necessary to desorb benzene completely after the adsorption at 0.1 atmosphere. This slow desorption is clearly due to the strong interaction between benzene and Ag. However, the bonds are of the order of 20 kcal/mol, which are weak enough so a substantial fraction of the adsorbed benzene is desorbed in a few minutes. For practical applications, thermal desorption may be a desirable option.

Pd-Y gave lower adsorption amounts than both Ag-Y and Na-Y. This decrease of adsorption amounts by ion-exchange with Pd was due to degradation of the zeolite structure. In Figure 26, the pore size distributions for all sorbents calculated from  $N_2$  isotherms at 77 K are shown. Pd-Y had a small pore volume with a wide pore size distribution, clearly indicating the collapse of the zeolite pore structure or pore blockage by Pd. The Pd ion-exchanged was performed at 80 °C, compared with the Ag ion-exchange at room temperature. Collapsing of zeolite structure tends to occur considerably more in acidic solution and at higher temperatures. The pore volume of Ag-Y also decreased by 23% after ion-exchange. However, this reduction of Ag-Y was mainly caused by 37% density increase of the zeolite lattice by replacing  $Na^+$  with  $Ag^+$

(27% reduction of pore volume per weight basis). The pore structure of Ag-Y was intact after ion-exchange.

Another interesting phenomenon in Figure 26 is the apparent shift of the pore size distribution in H-USY toward a higher value, compared to other zeolites. This was likely due to the lower polarizability of oxygen in the framework of high-SiO<sub>2</sub> zeolites (Pellenq and Nicholson, 1993), which will be discussed in detail in the section of Monte Carlo simulation results. Otherwise, the interactions between nitrogen and cations in zeolites would have led to a shift of the pore sizes toward smaller values for Na-Y, Ag-Y and Pd-Y. Since the pore sizes of Na-Y, Ag-Y and Pd-Y were the same as the actual value for Y zeolites (1.3nm), the latter explanation is not plausible.

### *Separation factors*

The pure component adsorption data were first fitted by both D-A (Dubinin-Astakhov) and L-F (Langmuir-Freundlich) isotherms. The separation factors of benzene over cyclohexane were then obtained using the equivalent multi-component isotherms. In the D-A equation of pure component gas, the volume adsorbed,  $V$ , at relative pressures  $P/P_s$  is expressed as

$$V = V_0 \exp \left[ - \left( C \ln \frac{P_s}{P} \right)^n \right] \quad (10)$$

where

$$C = \frac{RT}{\beta E_0} \quad (11)$$

Doong and Yang (Doong and Yang, 1988) extended the D-A equation to mixed-gas adsorption in a simple way by using the concept of maximum available pore volume without any additional equations such as the Lewis relationship (Lewis et al., 1950). For binary mixtures,

$$V_1 = (V_{01} - V_2) \exp \left[ - \left( C_1 \ln \frac{P_{s1}}{P_1} \right)^{n_1} \right] \quad (12)$$

$$V_2 = (V_{02} - V_1) \exp \left[ - \left( C_2 \ln \frac{P_{s2}}{P_2} \right)^{n_2} \right] \quad (13)$$

Since equation (12) and (13) are linear,  $V_1$  and  $V_2$  can be obtained in a straightforward fashion. After the calculation of  $V_1$  and  $V_2$ , volumetric adsorbed amounts were converted to molar

adsorbed amounts and the separation factors were calculated. The conversion of molar adsorbed amount to volumetric adsorbed amount and *vice versa* was performed using the liquid density data of the adsorbates. The liquid density at 120 and 180 °C were obtained by the modified Rackett equation by Spencer and Adler (Spencer and Adler, 1978). The liquid densities used in this work were 0.769 g/cc at 120 °C and 0.689 g/cc at 180 °C for benzene, and 0.679 g/cc at 120 °C and 0.606 g/cc at 180 °C for cyclohexane. The adsorbed molar volumes were assumed to be the same in both single- and mixed-gas adsorption.

For the Langmuir-Freundlich isotherm equation, pure component isotherm is written using three adjustable parameters:

$$q = \frac{q_0 B P^{1/n}}{1 + B P^{1/n}} \quad (14)$$

The L&F equation can also be extended for n-component mixture (Yang, 1987):

$$q_i = \frac{q_0 B_i P_i^{1/n_i}}{1 + \sum_{j=1}^n B_j P_j^{1/n_j}} \quad (15)$$

The fitting parameters for both isotherms are listed in Table 17 and the fitted curves are plotted in Figures 22 - 25. The separation factors of benzene over cyclohexane were calculated using the equilibrium mole fractions in adsorbed and gas phases:

$$\alpha = \frac{X_{\text{benzene}} / Y_{\text{benzene}}}{X_{\text{cyclohexane}} / Y_{\text{cyclohexane}}} \quad (16)$$

The calculated separation factors for Ag-Y and Na-Y are compared in Table 18. Both D-A and L-F equations led to similar dependence of separation factor on pressure. The separation factor for Ag-Y increased with decreasing concentration of benzene, while that for Na-Y at 180 °C decreased. Although the separation factors calculated by the two isotherms were not the same, the advantages of Ag-Y over Na-Y are clearly seen, especially at lower concentrations of benzene. This is certainly because Ag-Y can maintain its adsorption ability to benzene even at around  $1 \times 10^{-5}$  atm. On the other hand, at 0.01 and 0.001 atm of benzene and at the lower temperature of 120°C, Na-Y showed equivalent separation factors to Ag-Y.

For separations by adsorption and membranes, a separation factor of the order of 10 is considered high. For example, in air separation by pressure swing adsorption using zeolites and also by polymeric membranes, systems with separation factors ( $N_2/O_2$  for adsorption and  $O_2/N_2$  for membranes) of near 10 are commercially used. For aromatics/aliphatics separations using liquid membranes (e.g., toluene/heptane and benzene/heptane separations), separation factors of the order of 10-100 yielded excellent separations (Li, 1968; Li, 1971). The separation factors shown in Table 18, in the order of 10-10,000, are excellent for separation/purification.

### ***Diffusion time constants***

In Table 19, diffusion time constants calculated from 0 - 0.3 fractional uptake were summarized. Diffusion time constants of benzene and cyclohexane in Na-Y and Ag-Y were of the order of  $10^{-4}$  1/s. These values were almost the same as those of benzene and cyclohexane into  $AgNO_3$  monolayer dispersed  $SiO_2$  sorbent (Takahashi et al.). However, these values were an order of magnitude lower than those of propylene and propane in  $AgNO_3$  monolayer-dispersed  $SiO_2$  sorbent (Rege, 1998) and at least the same as those of ethylene and ethane into Ag ion-exchanged resins (Wu et al., 1997). The diffusion rates of benzene in these zeolites are high for applications (Yang, 1987).

### **Molecular Orbital Calculation**

#### ***Adsorption Bond Energy and Molecular Geometries***

Adsorption energy and structural geometry were calculated using molecular orbital theory. The calculated heat of adsorption using B3LYP/3-21G level by equation (1) is also compared with experimental and Monte Carlo simulation results in Table 16. The theoretical value, 17.2 kcal/mol, was in fairly good agreement with the experimental value. The comparison of bond length by benzene adsorption revealed that the Ag-O length increased from 3.023Å to 3.246Å. The C-C bond length in benzene also increased from 1.385Å to 1.385-1.391Å. This trend was consistent with that for benzene interaction with AgCl (Takahashi et al.).

#### ***Natural Bond Orbital (NBO) Results***

The nature of benzene-Ag zeolite interaction can be better understood by analyzing the NBO results. The main feature of the interaction can be seen from the population changes in the vacant outer-shell s orbital of the silver and those in the d orbitals of silver upon adsorption. In Table 20, NBO analysis results for benzene on Ag zeolite are compared with other

combinations of adsorbates and adsorbents. According to the electron population changes by benzene adsorption on Ag zeolite, the trend is in agreement with previously reported trend of  $\pi$ -complexation (Cheng, 1996; Huang et al., 1999a; 1999b; 1999c ; Takahashi et al.) i.e., donation of electron charges from the p-orbitals of benzene to the vacant s-orbital of the silver ( $\sigma$  donation) and, simultaneously, back donation of electron charges from the d-orbitals of silver to  $\pi^*$  orbital of benzene ( $d-\pi^*$  back donation). The contribution of  $d-\pi^*$  back donation is larger than  $\sigma$  donation, resulting in the decrease of net electron charge in silver. The net electron charge of carbon in benzene increased instead.

The differences of electron population changes between benzene and ethylene adsorption deserve a discussion. From Table 20, it is seen that the contribution of  $\sigma$  donation is predominant in ethylene adsorption, while  $d-\pi^*$  back donation is slightly larger in benzene adsorption. Also, the extent of  $\sigma$  donation and  $d-\pi^*$  back donation by benzene adsorption was considerably smaller compared with ethylene adsorption. Therefore,  $\pi$ -complexation with benzene was weaker than that with ethylene. Weak  $\pi$ -complexation of benzene can also be understood by the difference in bond lengths. The bond length between carbon in ethylene and silver in AgCl was 2.66 Å (Huang et al., 1999b), while that between carbon in benzene and silver in Ag zeolite or AgCl was 2.71-3.7 Å or 3.22 Å (Takahashi et al.), respectively. This longer bond length was caused by the less overlap of orbitals from the weaker  $\pi$ -complexation.

### Monte Carlo Simulation

Monte Carlo simulation of adsorption isotherms provides great insight into the adsorption mechanism via model construction, charge assignment and forcefield determination. In this section, benzene adsorption on Na-Y, H-USY and Ag-Y is simulated and the mechanism of adsorption on each zeolite is discussed.

#### *Na-Y zeolite*

GCMC simulation results of benzene isotherms at 120 and 180°C using the potential parameters given in Table 15 are shown in Figure 27, where they are also compared with experimental data. The simulation results were in excellent agreement with experimental data. The calculated heats of adsorption were 16.4 - 18.5 kcal/mol, which were in agreement with that from experiments. It was hence confirmed that the energy expressions and parameters were suitable for simulation of benzene isotherms on Na-Y.

### *H-USY zeolite*

First, simulation of benzene isotherms on H-USY was attempted using the same potential parameters as on Na-Y. However, the simulated isotherms were considerably higher than the experimental data. This disagreement was caused by incorrect well depth parameters,  $\epsilon_{O-C}$  and  $\epsilon_{O-H}$ , for van der Waals interaction. Pellenq and Nicholson (Pellenq and Nicholson, 1993) reported the values of the polarizabilities of framework atoms in silicalite and aluminosilicates determined from Auger electron spectroscopy data. It was found that the polarizability for oxygen in zeolite framework is sensitive to the ratio of silicon to aluminum and also the nature of the extraframework cations. Watanabe et al. (Watanabe et al., 1995) used different potential values for oxygen in silicalite (0.202 kcal/mol), denoted by  $Oz(Si-O-Si)$ , and that in aluminosilicates (0.334 kcal/mol), denoted by  $Oz(Si-O-Al)$ .

In this work, an adjustment of  $\epsilon_{Oz(Si-O-Si)-C}$  and  $\epsilon_{Oz(Si-O-Si)-H}$  was made to simulate the experimental Henry's law constants at 120 and 180 °C. Here since low pressure data depend only on the benzene-zeolite interactions so the benzene-benzene interactions were neglected. Using the well depth parameter for  $\epsilon_{Na-C} = 0.04187$  kcal/mol and  $\epsilon_{Na-H} = 0.03153$  kcal/mol for Na-Y (in Table 15) and assuming  $\epsilon_{Na} = 0.041$  kcal/mol as used by Watanabe et al. (Watanabe et al., 1995) for Na-A and Na-X,  $\epsilon_C = 0.0428$  kcal/mol and  $\epsilon_H = 0.0243$  kcal/mol were obtained from the geometric combination rule, equation (9). Therefore,  $\epsilon_{Oz(Si-O-Si)-C}$  and  $\epsilon_{Oz(Si-O-Si)-H}$  for H-USY could be expressed as  $(0.0428 \times \epsilon_{Oz(Si-O-Si)})^{0.5}$  and as  $(0.0243 \times \epsilon_{Oz(Si-O-Si)})^{0.5}$ , respectively. By fitting with  $\epsilon_{Oz(Si-O-Si)}$ ,  $\epsilon_{Oz(Si-O-Si)} = 0.665$  kcal/mol was obtained to fit the experimental Henry's law constant of 0.519 molecules/(cell.kPa) at 120 °C and 0.137 molecules/(cell.kPa) at 180 °C. The ratio of  $\epsilon_{Oz(Si-O-Si)}$  over  $\epsilon_{Oz(Si-O-Al)}$  was 0.44 (calculated from  $\epsilon_{Oz(Si-O-Al)-H}$ ) - 0.60 (calculated from  $\epsilon_{Oz(Si-O-Al)-C}$ ), which was in agreement with the ratio of 0.60 obtained by Watanabe et al. (Watanabe et al., 1995).

Using the modified parameters for H-USY (in Table 15), the benzene isotherms were calculated and compared with experimental isotherms in Figure 28. Again, the isotherms and the heat of adsorption (8.2 - 9.2 kcal/mol) obtained from simulation were in excellent agreement with the experimental data.



*Ag-Y zeolite*

The potential parameters for Ag-Y are listed in Table 15. These parameters were modified to get the low pressure points of the isotherm at 180 °C (1.30 mmol/g at  $1.6 \times 10^{-4}$  atmosphere), although adjustment of the parameters to fit the experimental Henry's law constant was preferable. The reason not to use the experimental Henry's constant was that the small pressure values ( $8.7 \times 10^{-6}$  atmosphere) at the lowest adsorbed amount in the isotherms might lead to the large error of potential parameters. The procedure of adjustment was basically the same as in the case for H-USY except for changing the  $\epsilon_{Ag}$  value instead of the  $\epsilon_{Oz(Si-O-Si)}$  value.  $\epsilon_C = 0.0428$  kcal/mol and  $\epsilon_H = 0.0243$  kcal/mol were obtained from the geometric combination rule, equation (9). Then,  $\epsilon_{Ag-C}$  and  $\epsilon_{Ag-H}$  for Ag-Y could be estimated from  $(0.0428 \times \epsilon_{Ag})^{0.5}$  and  $(0.0243 \times \epsilon_{Ag})^{0.5}$ , respectively. In **Case I** for Ag-Y,  $\epsilon_{Ag}$  became 14.3 kcal/mol, while  $\epsilon_{Ag} = 13.5$  kcal/mol was obtained for **Case II**. The larger well-depth parameter was needed for Case I to compensate for the weaker Coulombic interaction due to the smaller Ag cation charge. In both cases, the  $\epsilon_{Ag}$  values used were more than 2 orders of magnitude greater than  $\epsilon_{Na}$ , clearly indicating the strong interaction from  $\pi$ -complexation.

Figure 29 shows the simulation results of benzene on Ag-Y for Case I and Case II. The differences between Case I and Case II were fairly small. In both cases, the agreement with experimental isotherms was not as good as that for Na-Y and H-USY. However, they certainly followed the basic trend of the experimental isotherms. The calculated heat of adsorption was 18.8 - 21.1 kcal/mol, which was higher than Na-Y and also in agreement with the experimental value.

In all cases, not only Ag-Y but also Na-Y and H-USY, the simulated isotherms tended to be higher than the experimental isotherms in the lower pressure range with few exceptions, while they were lower in the higher pressure range. The higher simulation results at low pressures might be caused by the larger values for the well-depth parameter between oxygen (zeolite) - carbon (benzene) interaction and oxygen (zeolite) - hydrogen (benzene) interaction. The other possible cause was the imperfection of the zeolite crystals. Since zeolites contain defects while in Monte Carlo simulation perfect zeolite lattice was assumed. In the high pressure range, larger experimental values were possibly caused by adsorption between zeolite crystals.

Adsorption sites for benzene on Na-Y and Ag-Y were investigated using the Mass Cloud Plots function in Cerius2 (not shown here). It was confirmed that benzene was adsorbed preferentially near the SII cation sites and the center of the 12-ring window, which was consistent with the neutron diffraction data for Na-Y obtained by Fitch (Fitch et al., 1986). For Ag-Y, benzene was adsorbed slightly further away from the SII cation sites than that in Na-Y, due to the fact that the van der Waals radius of  $\text{Ag}^+$  is 30% larger than that of  $\text{Na}^+$ .

### Notation

A = repulsive parameter for Buckingham potential

B = repulsive parameter for Buckingham potential or Langmuir constant

C = dispersive parameter for Buckingham potential or constant for D-A equation

D = diffusivity

E = energy

n = constant

P = pressure

q = point charge or molar adsorbed amount

R = van der Waals radii or gas constant

r = distance or radius

T = temperature

U = potential energy

V = volumetric adsorbed amount

X = equilibrium mole fraction in adsorbed phase

Y = equilibrium mole fraction in gas phase

### Greek letters

$\alpha$  = polarizability or separation factor

$\beta$  = adjustable parameter

$\epsilon$  = well depth parameter for Lennard-Jones potential

$\sigma$  = distance parameter for Lennard-Jones potential

### Subscript

i = atom site or component

j = atom site or component

s = saturation

Table 15 The Potential Parameters used for Na-Y, Ag-Y and H-USY

| Na-Y      | $U_{AA}^{1)}$            | C-C           | H-H           | C-H           |               |
|-----------|--------------------------|---------------|---------------|---------------|---------------|
|           | A (kcal/mol)             | 88371         | 2861          | 15901         |               |
|           | B (1/A)                  | 3.60          | 3.74          | 3.67          |               |
|           | C ( $A^6$ *kcal/mol)     | 583.13        | 32.60         | 137.88        |               |
|           | $U_{AZ}$                 | O-C           | O-H           | Na-C          | Na-H          |
|           | $\varepsilon$ (kcal/mol) | 0.25547       | 0.16515       | 0.04187       | 0.03153       |
|           | $\sigma$ (Å)             | 2.9984        | 2.5893        | 3.3279        | 2.7651        |
| Ag-Y      | $U_{AZ}$                 | O-C           | O-H           | Ag-C          | Ag-H          |
| (Case I)  | $\varepsilon$ (kcal/mol) | 0.25547       | 0.16515       | <u>0.7823</u> | <u>0.5895</u> |
|           | $\sigma$ (Å)             | 2.9984        | 2.5893        | <u>3.5773</u> | <u>3.0145</u> |
| Ag-Y      | $U_{AZ}$                 | O-C           | O-H           | Ag-C          | Ag-H          |
| (Case II) | $\varepsilon$ (kcal/mol) | 0.25547       | 0.16515       | <u>0.7601</u> | <u>0.5728</u> |
|           | $\sigma$ (Å)             | 2.9984        | 2.5893        | <u>3.5773</u> | <u>3.0145</u> |
| H-USY     | $U_{AZ}$                 | O-C           | O-H           |               |               |
|           | $\varepsilon$ (kcal/mol) | <u>0.1687</u> | <u>0.1271</u> |               |               |
|           | $\sigma$ (Å)             | 2.9984        | 2.5893        |               |               |

1) Parameters for  $U_{AA}$  are the same for all sorbents.

2) The numbers with underline were determined in this work.

Table 16 Comparison of Heat of Adsorption (kcal/mol)  
between Experimental and Simulated Results

|             |                                 | Na-Y      | Ag-Y      | H-USY   |
|-------------|---------------------------------|-----------|-----------|---------|
| Benzene     | Experimental                    | 17.7-18.2 | 20.5-20.7 | 6.2-7.2 |
|             | Monte Carlo Simulation          | 16.4-18.5 | 18.8-21.1 | 8.2-9.2 |
|             | Molecular Orbital Calculation   | ***       | 17.2      | ***     |
|             | Barthomeuf et al. <sup>1)</sup> | 17.5-18.0 | ***       | ***     |
| Cyclohexane | Experimental                    | 10.9-13.0 | 12.1-12.3 | 4.1-4.3 |
|             | Barthomeuf et al. <sup>1)</sup> | 12.0-13.2 | ***       | ***     |

1) Barthomeuf and Ha, 1973

Table 17 Parameters for the D-A and L-F Equations

| Adsorbent | Adsorbate   | Temp. (°C) | D-A Equation |       |      |       | L-F Equation |         |      |
|-----------|-------------|------------|--------------|-------|------|-------|--------------|---------|------|
|           |             |            | $V_0$        | C     | n    | $P_s$ | $q_b$        | B       | n    |
|           |             |            | (cc/g)       | (-)   | (-)  | (atm) | (mmol/g)     | (1/atm) | (-)  |
| Na-Y      | Benzene     | 120        | 0.295        | 0.092 | 3.76 | 2.96  | 3.15         | 30.7    | 2.53 |
|           | Benzene     | 180        | 0.326        | 0.120 | 4.73 | 10.07 | 2.82         | 449     | 0.9  |
|           | Cyclohexane | 120        | 0.267        | 0.149 | 5.01 | 2.84  | 2.58         | 51.2    | 1.18 |
|           | Cyclohexane | 180        | 0.264        | 0.168 | 6.44 | 9.48  | 2.30         | 61.9    | 0.77 |
| Ag-Y      | Benzene     | 120        | 0.244        | 0.056 | 1.57 | 2.96  | 3.07         | 3.67    | 7.46 |
|           | Benzene     | 180        | 0.248        | 0.082 | 3.05 | 10.07 | 2.03         | 156     | 1.85 |
|           | Cyclohexane | 120        | 0.225        | 0.133 | 4.32 | 2.84  | 2.02         | 48.4    | 1.44 |
|           | Cyclohexane | 180        | 0.237        | 0.145 | 4.96 | 9.48  | 1.80         | 74.3    | 0.91 |
| H-USY     | Benzene     | 120        | 0.237        | 0.318 | 2.84 | 2.96  | 3.40         | 11.2    | 0.62 |
|           | Benzene     | 180        | 0.234        | 0.333 | 2.17 | 10.07 | 3.40         | 1.11    | 0.74 |
|           | Cyclohexane | 120        | 0.249        | 0.265 | 5.85 | 2.84  | 1.33         | 2500000 | 0.2  |
|           | Cyclohexane | 180        | 0.15         | 0.232 | 4.93 | 9.48  | 0.73         | 260     | 0.39 |
| Pd-Y      | Benzene     | 120        | 0.173        | 0.237 | 2.15 | 2.96  | 0.883        | 240     | 0.7  |
|           | Cyclohexane | 120        | 0.16         | 0.317 | 1.34 | 2.84  | 0.753        | 9.22    | 1.2  |

Table 18 Separation Factors estimated by the D-A and L&amp;F Equations

| Pressure (atm) |             | Temp. (°C) | D-A Equation |      | L-F Equation |      |
|----------------|-------------|------------|--------------|------|--------------|------|
| Benzene        | Cyclohexane |            | Ag-Y         | Na-Y | Ag-Y         | Na-Y |
| 0.01           | 1           | 120        | 107          | ***  | 6            | 12   |
| 0.001          | 1           | 120        | 416          | 441  | 45           | 48   |
| 0.0001         | 1           | 120        | 2286         | 1016 | 335          | 191  |
| 0.00001        | 1           | 120        | 14361        | 2553 | 2462         | 767  |
| 0.01           | 1           | 180        | 39           | 95   | 19           | 5.4  |
| 0.001          | 1           | 180        | 120          | 71   | 57           | 4.2  |
| 0.0001         | 1           | 180        | 456          | 26   | 163          | 3.3  |
| 0.00001        | 1           | 180        | 1767         | 0.5  | 470          | 2.6  |

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Table Diffusion Time Constants of Benzene and Cyclohexane

| Adsorbents  | emp.<br>(°C)  | Benzene (Pressure Change)   |   | Cyclohexane (Pressure Change) |   |
|---|---------------|-----------------------------|---|-------------------------------|---|
|   |               | (1/s)                       | (atm)   | (1/s)                         | (atm)   |
| Na-Y  | 120           | $2.1 \times 10^{-4}$        | $(5.4 \times 10^{-3} \rightarrow 2.6 \times 10^{-2})$ | $9.8 \times 10^{-4}$          | $(1.1 \times 10^{-2} \rightarrow 2.0 \times 10^{-2})$ |
| Ag-Y  | 120           | $4.2 \times 10^{-4}$        | $(5.4 \times 10^{-3} \rightarrow 2.6 \times 10^{-2})$ | $1.1 \times 10^{-4}$          | $(1.1 \times 10^{-2} \rightarrow 2.0 \times 10^{-2})$ |
| AgNO <sub>3</sub> /SiO <sub>2</sub> (0.33g/g) <sup>1)</sup> | 120           | $1.3 \times 10^{-4}$        | $(2.0 \times 10^{-3} \rightarrow 3.7 \times 10^{-2})$ | $2.9 \times 10^{-4}$          | $(2.0 \times 10^{-3} \rightarrow 3.7 \times 10^{-2})$ |
| Adsorbents  | Temp.<br>(°C) | propylene (Pressure Change) |   | Propane (Pressure Change)     |   |
|   |               | (1/s)                       | (atm)   | (1/s)                         | (atm)   |
| AgNO <sub>3</sub> /SiO <sub>2</sub> (0.33g/g) <sup>2)</sup> | 70            | $3.5 \times 10^{-3}$        | (0→1)   | ***                           | ***   |
| Ag-Amberlyst-35 <sup>3)</sup>                               | 70            | $1.5 \times 10^{-4}$        | ***   | $1.4 \times 10^{-4}$          | ***   |

1) Takahashi et al., 2000

2) Rege et al., 1998

3) Wu et al., 1997

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 Table Summary of the NBO Analysis of the  $\pi$ -complexation:  
 Electron Population Changes of Each Orbital after Adsorption

| Method / BasisSet  | Silver  |             |            | Carbon  |             |            |
|--|---------|-------------|------------|---------|-------------|------------|
|  | 5S      | $\Sigma 4d$ | Net Change | 2s      | $\Sigma 2p$ | Net Change |
| benzene on Ag Zeolite B3LYP/3-21G                                  | 0.00541 | -0.0135     | -0.00805   | 0.00554 | 0.00709     | 0.01263    |
| Benzene on AgCl <sup>1</sup> B3LYP/LanL2DZ                         | 0.0033  | -0.0071     | -0.0038    | ***     | ***         | ***        |
| C <sub>2</sub> H <sub>4</sub> on Ag Zeolite <sup>2</sup> MP2/3-21G | 0.0596  | -0.0177     | 0.0419     | 0.0203  | 0.0193      | 0.0396     |
| C <sub>2</sub> H <sub>4</sub> on AgCl <sup>2)</sup> MP2/3-21G      | 0.1204  | -0.0470     | 0.0734     | 0.0226  | 0.0142      | 0.0368     |
| C <sub>2</sub> H <sub>4</sub> on AgCl <sup>3)</sup> B3LYP/LanL2DZ  | 0.061   | -0.055      | 0.006      | ***     | ***         | ***        |

1) Takahashi et al., 2000

2) Chen and Yang, 1996

3) Huang et al., 1999



### EXAMPLES OF SOME SUITABLE ADSORBENTS

A brief description of some non-limitative examples of adsorbents which may successfully be used in the present invention follows. Detailed descriptions may be found in U.S. Patent No. 6,423,881, and in U.S. Patent No. 6,515,037, each of which applications is incorporated herein by reference in its entirety.

The adsorbent comprises a carrier having a surface area, the carrier having dispersed thereon a monolayer of a d-block transition metal compound, eg. a silver compound. The silver compound releasably retains the thiophenes; and the carrier comprises a plurality of pores having a pore size greater than the effective molecular diameter of the thiophenes.

It is to be understood that any suitable carrier may be used. However, in a preferred embodiment, the carrier has a BET surface area greater than about 50 square meters per gram and up to about 2,000 square meters per gram, and comprises a plurality of pores having a pore size greater than about 3 angstroms and up to about 10 microns. In a more preferred embodiment, the carrier is a high surface area support selected from the group consisting of refractory inorganic oxide, molecular sieve, activated carbon, and mixtures thereof. Still more preferred, the carrier is a refractory inorganic oxide selected from the group consisting of pillared clay, alumina and silica.

It is also to be understood that any suitable silver compound may be used. However, in a preferred embodiment, the silver compound is a silver (I) halide. In a more preferred embodiment, the silver compound is a silver salt, and the salt is selected from the group consisting of acetate, benzoate, bromate, chlorate, perchlorate, chlorite, citrate, fluoride, nitrate, nitrite, sulfate, and mixtures thereof.

In one exemplary embodiment of this embodiment of the present invention, the silver compound is silver nitrate ( $\text{AgNO}_3$ ) and the carrier is silica ( $\text{SiO}_2$ ).

The method of the present invention may further comprise the step of changing at least one of the pressure and temperature to thereby release the thiophenes-rich component from the adsorbent. It is to be understood that the pressures and temperatures used may be within a suitable range. However, in the preferred embodiment, the selected pressure of preferential adsorption is a first pressure, and the pressure of release is a second pressure less than the first pressure. In a more preferred embodiment, the first pressure is in a range of about 1 atmosphere to about 35 atmospheres, and the second pressure is in a range of about 0.01 atm to about 5 atm.

In the preferred embodiment, the selected temperature of preferential adsorption is a first temperature, and the temperature of release is a second temperature greater than the first temperature. In a more preferred embodiment, the first temperature is in a range of about 0°C to about 50°C, and the second temperature is in a range of about 70°C to about 200°C.

Without being bound to any theory, it is believed that the retaining of the thiophenes is accomplished by formation of  $\pi$ -complexation bonds between the silver compound and the thiophenes. Separation by  $\pi$ -complexation is a subgroup of chemical complexation where the mixture is contacted with a second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound. At the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature or decreasing the pressure.

15           The  $\pi$ -complexation generally pertains to the main group (or d-block) transition metals, that is, from Sc to Cu, Y to Ag, and La to Au in the periodic table. These metals or their ions can form the normal  $\sigma$  bond to carbon and, in addition, the unique characteristics of the d orbitals in these metals or ions can form bonds with the unsaturated hydrocarbons (olefins) in a nonclassic manner. This type of bonding is broadly referred to as  $\pi$ -complexation, and has been considered for gaseous hydrocarbon separation and purification using cumbersome liquid solutions.

A further example of an adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites have a d-block transition metal cation, eg. silver cation or copper cation, present. In the more preferred embodiment, the cationic sites of the ion-exchanged zeolite contain silver cation. In a further preferred embodiment, essentially all cationic sites of the ion-exchanged zeolite contain the silver cation.

Without being bound to any theory, it is believed that the preferential adsorption occurs by  $\pi$ -complexation.

Figs. 30-32 are graphs depicting further breakthrough curves.

While preferred embodiments of the invention have been described in detail, it will be apparent to those skilled in the art that the disclosed embodiments may be modified. Therefore, the foregoing description is to be considered exemplary rather than limiting, and the true scope of the invention is that defined in the following claims.

What is claimed is:

1. A process for removing thiophene and thiophene compounds from liquid fuel, the method comprising the step of:

contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and a thiophene/thiophene compound-rich adsorbed component, wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites having d-block transition metal cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation.

2. A process for removing thiophene and thiophene compounds from liquid fuel, the method comprising the steps of:

contacting the liquid fuel with an adsorbent which preferentially adsorbs the thiophene and thiophene compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and a thiophene/thiophene compound-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a d-block transition metal compound dispersed on substantially the entire surface area, the metal compound releasably retaining the thiophene/thiophene compounds; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the thiophene/thiophene compounds; and

25 changing at least one of the pressure and temperature to thereby release the thiophene/thiophene compound-rich component from the adsorbent.

3. The process as defined in claim 1 wherein at  $10^{-5}$  atm, the adsorbent adsorbs more than 1 mmol/gram of thiophene.

30

4. The process as defined in claim 2 wherein at  $10^{-5}$  atm, the adsorbent adsorbs more than 1 mmol/gram of thiophene.

5. A process for removing aromatic compounds from liquid fuel, the method comprising the step of:

contacting the liquid fuel with an adsorbent which preferentially adsorbs the aromatic compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and an aromatic compound-rich adsorbed component,

wherein the adsorbent comprises an ion-exchanged zeolite selected from the group consisting of zeolite X, zeolite Y, zeolite LSX, and mixtures thereof, the zeolite having exchangeable cationic sites, and at least some of the sites having d-block transition metal cation present, and wherein the preferential adsorption occurs by  $\pi$ -complexation.

6. A process for removing aromatic compounds from liquid fuel, the method comprising the steps of:

10     contacting the liquid fuel with an adsorbent which preferentially adsorbs the aromatic compounds, at a selected temperature and pressure, thereby producing a non-adsorbed component and an aromatic compound-rich adsorbed component; the adsorbent comprising a carrier having a surface area, the carrier having a monolayer of a d-block transition metal compound dispersed on substantially the entire surface area, the metal compound releasably retaining the aromatic compounds; and the carrier comprising a plurality of pores having a pore size greater than the effective molecular diameter of the aromatic compounds; and

          changing at least one of the pressure and temperature to thereby release the aromatic compound-rich component from the adsorbent.

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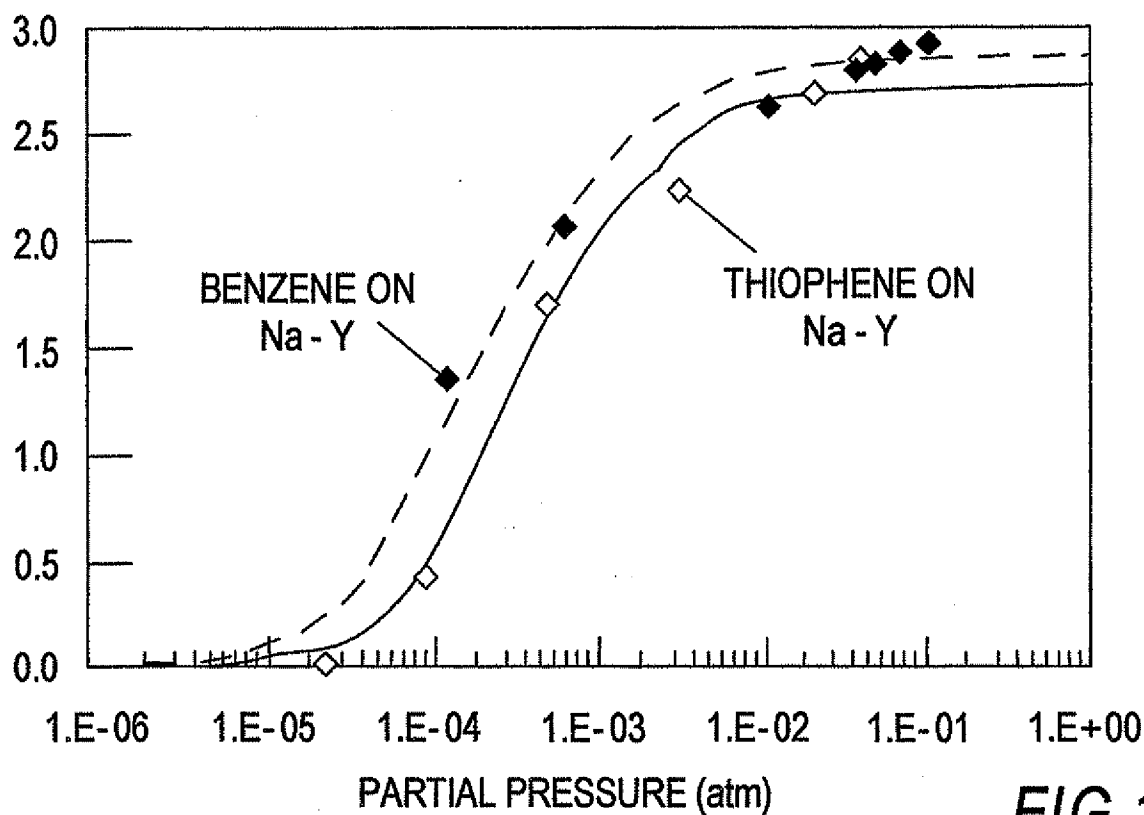


FIG 1

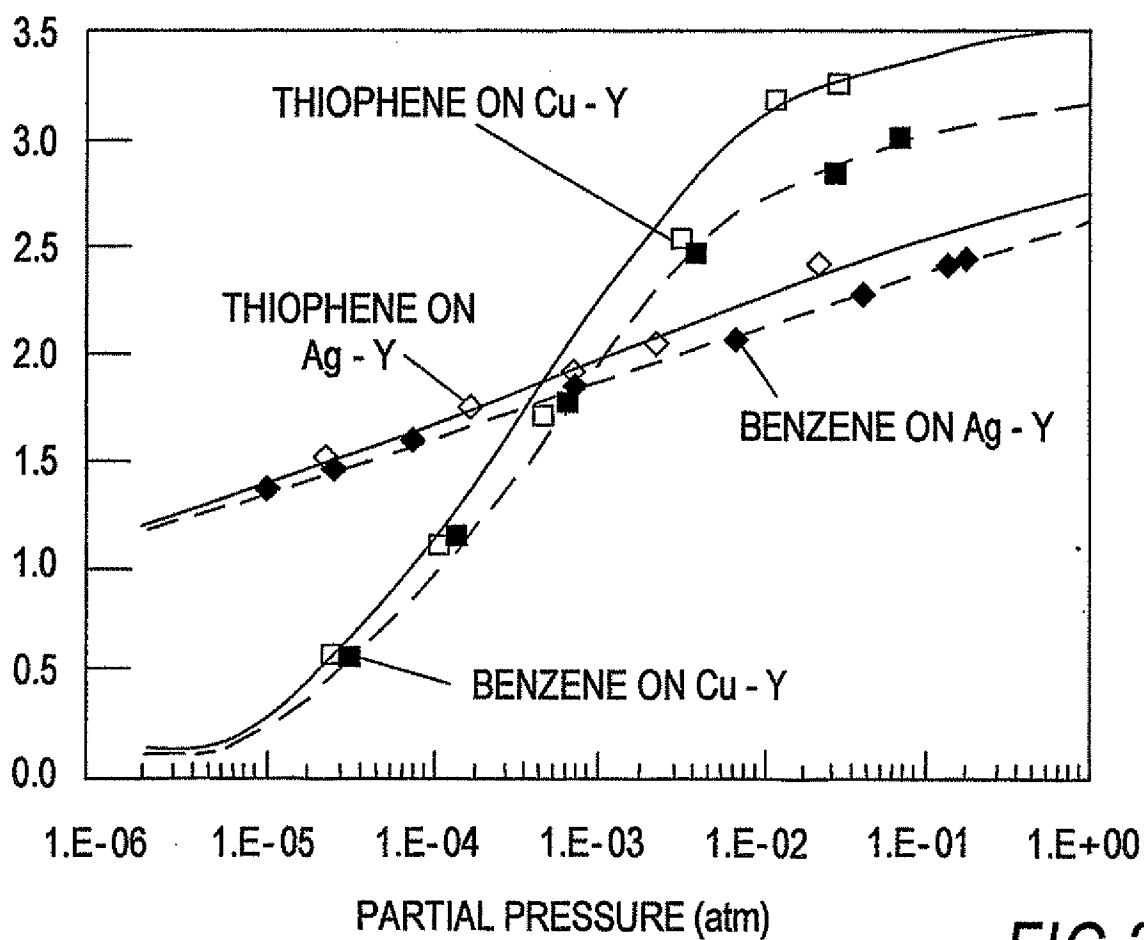


FIG 2

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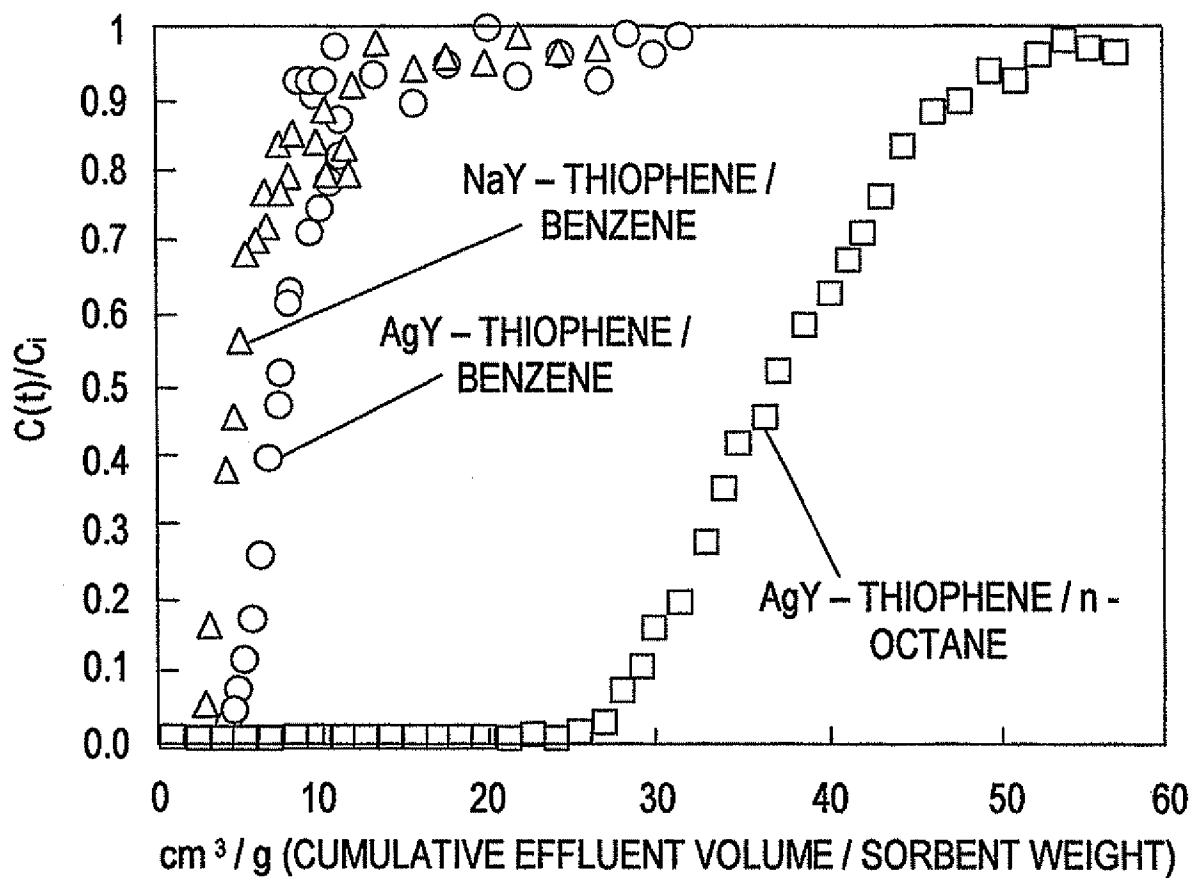


FIG 3

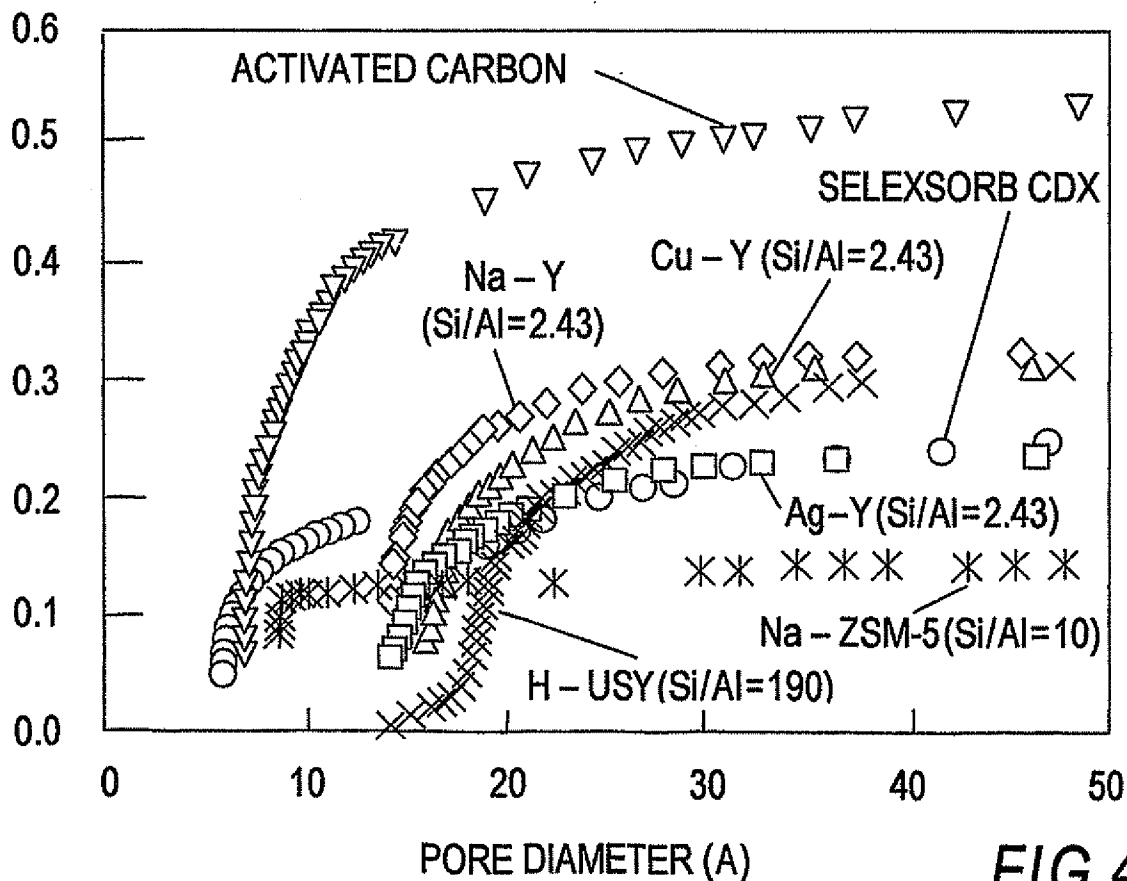


FIG 4

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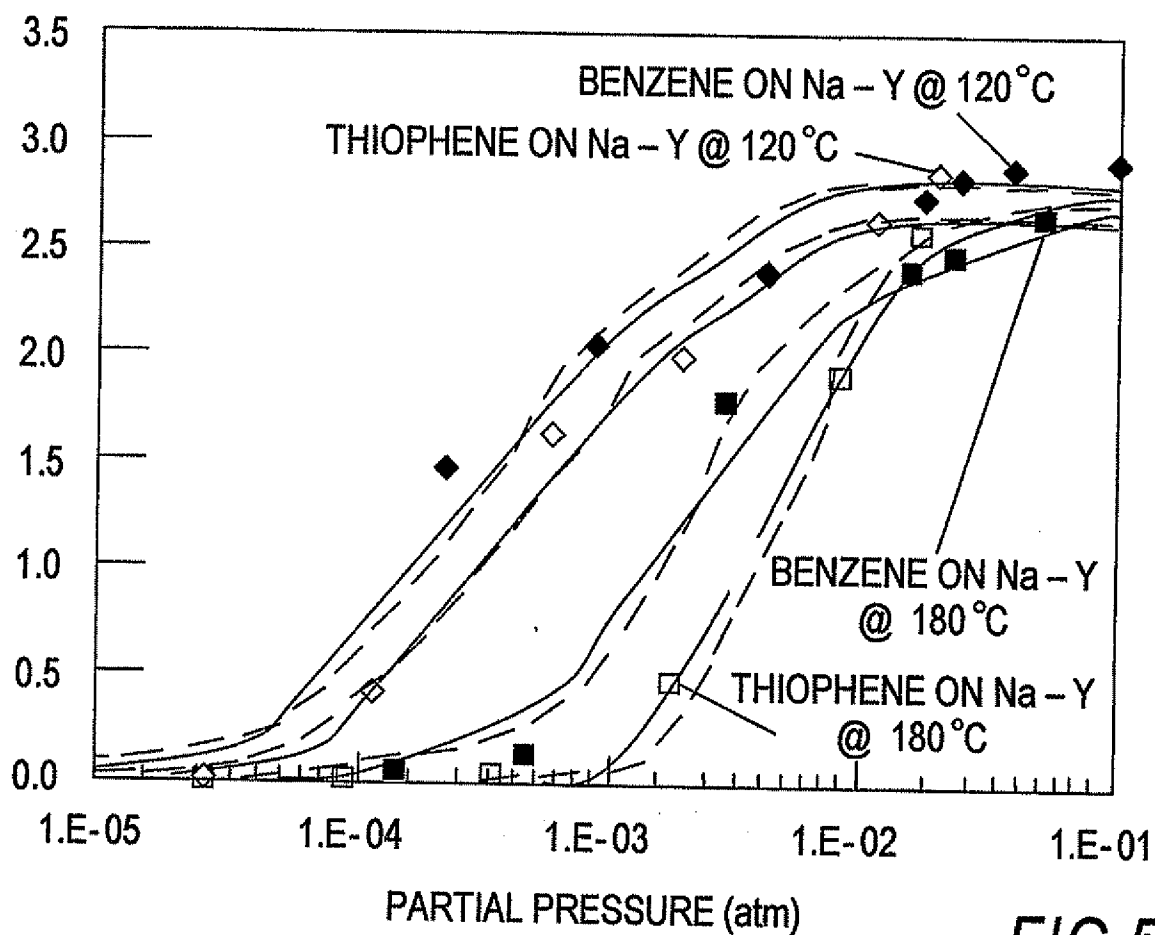


FIG 5

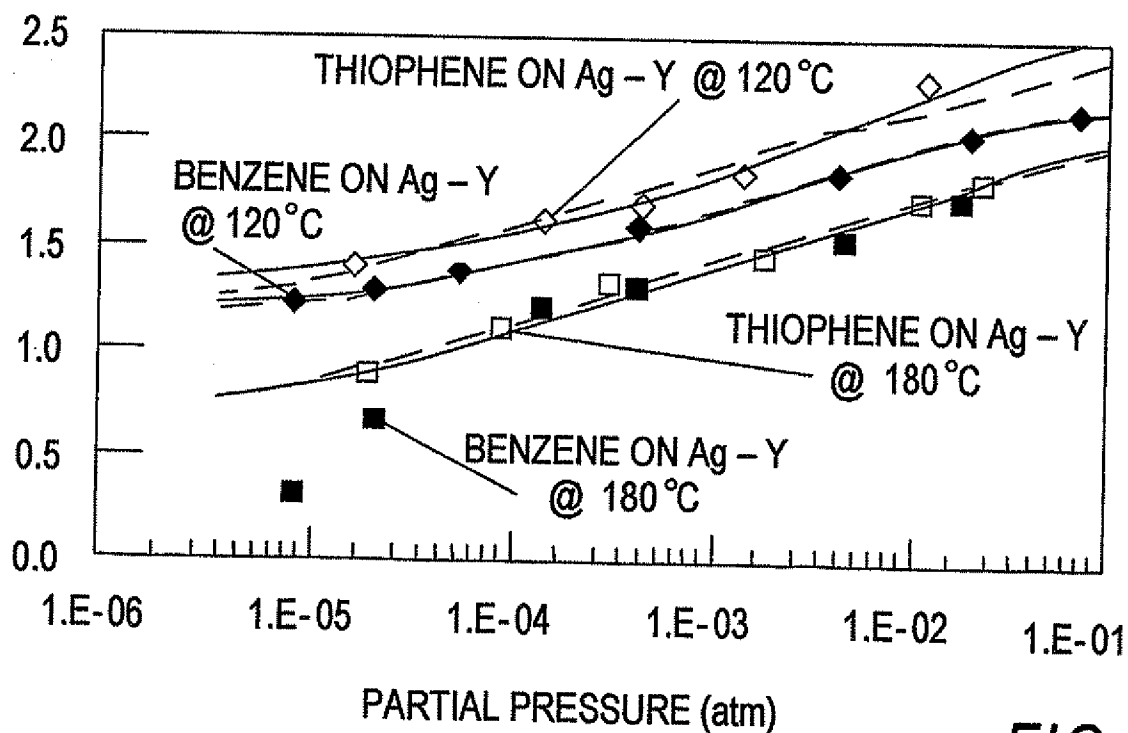


FIG 6

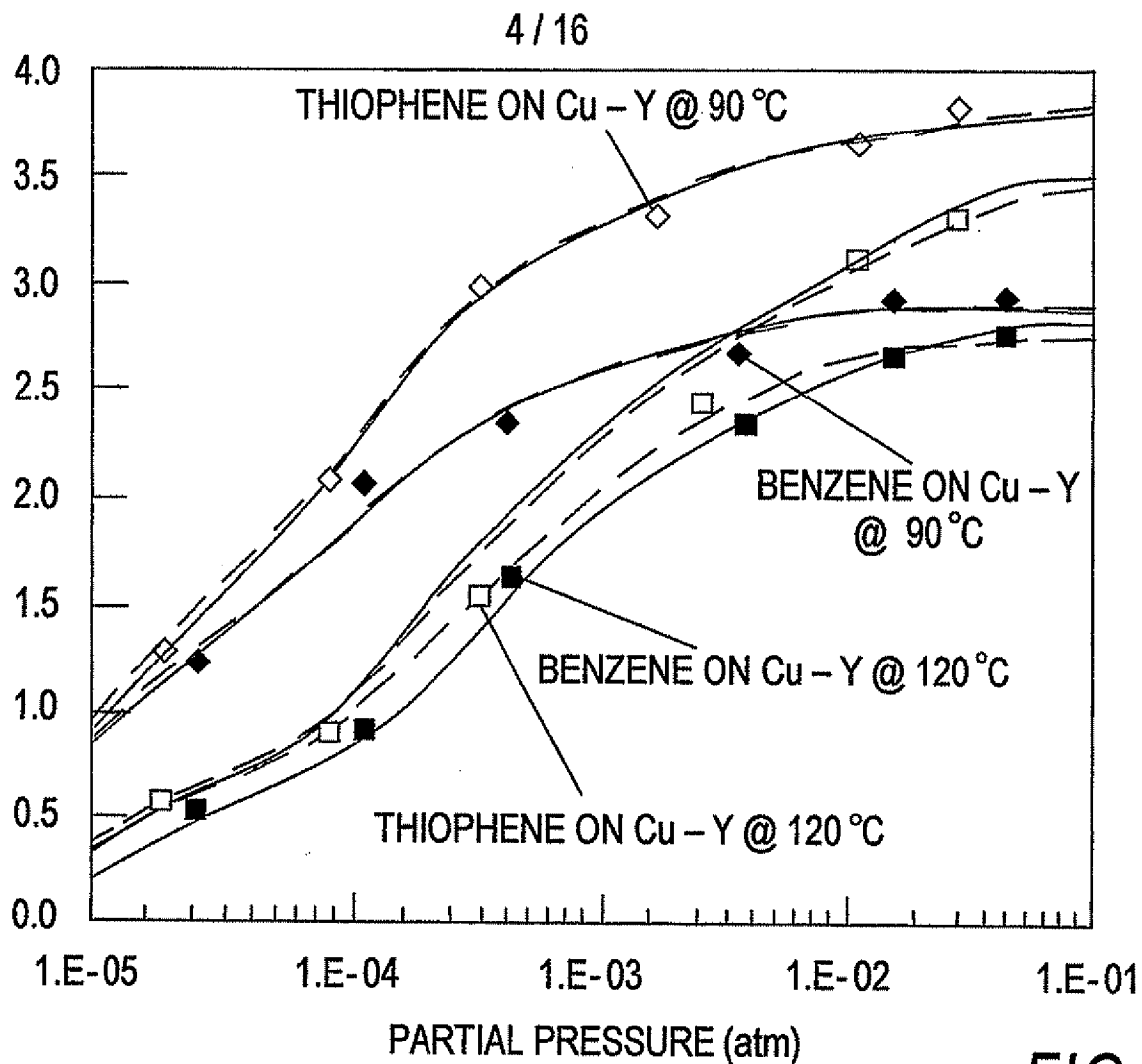


FIG 7

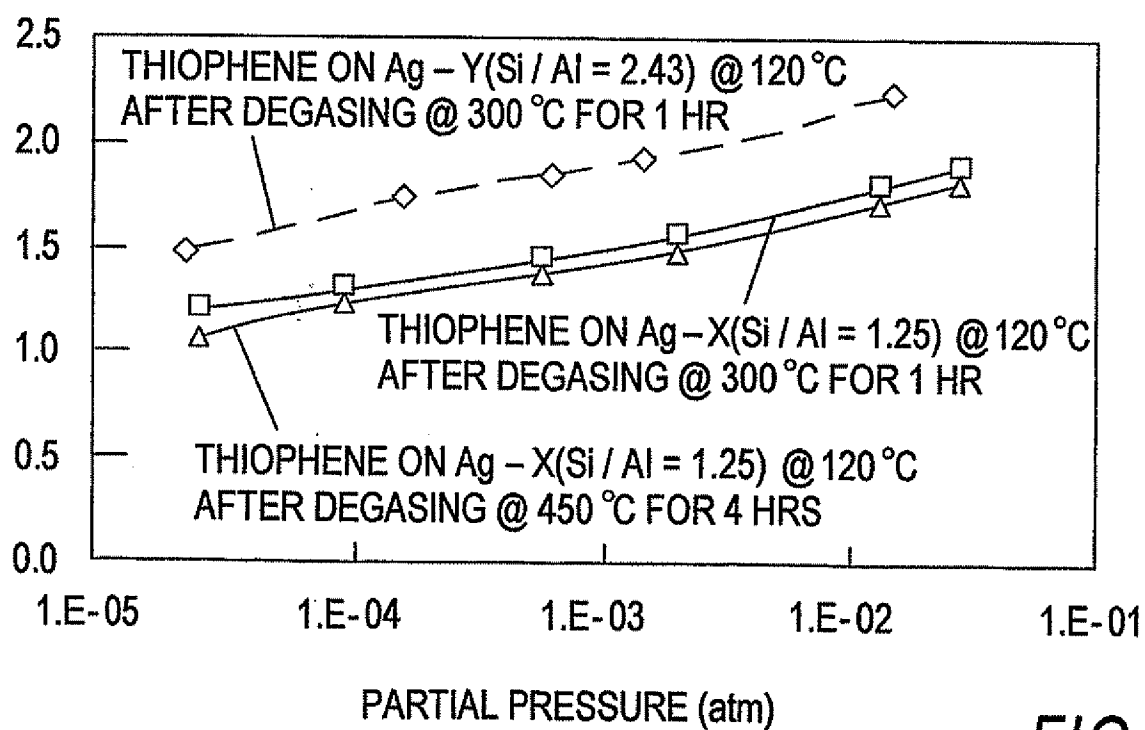


FIG 8



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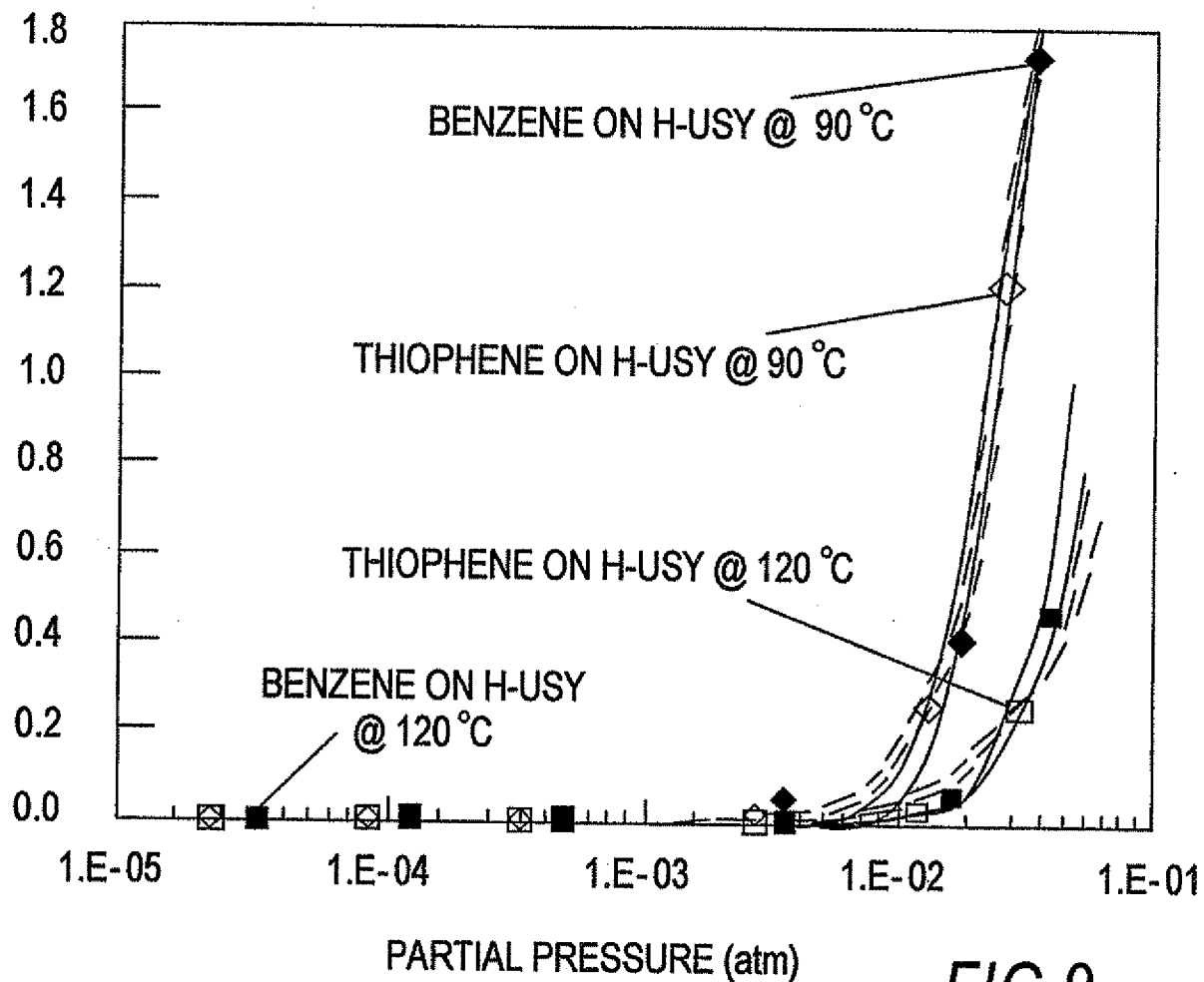


FIG 9

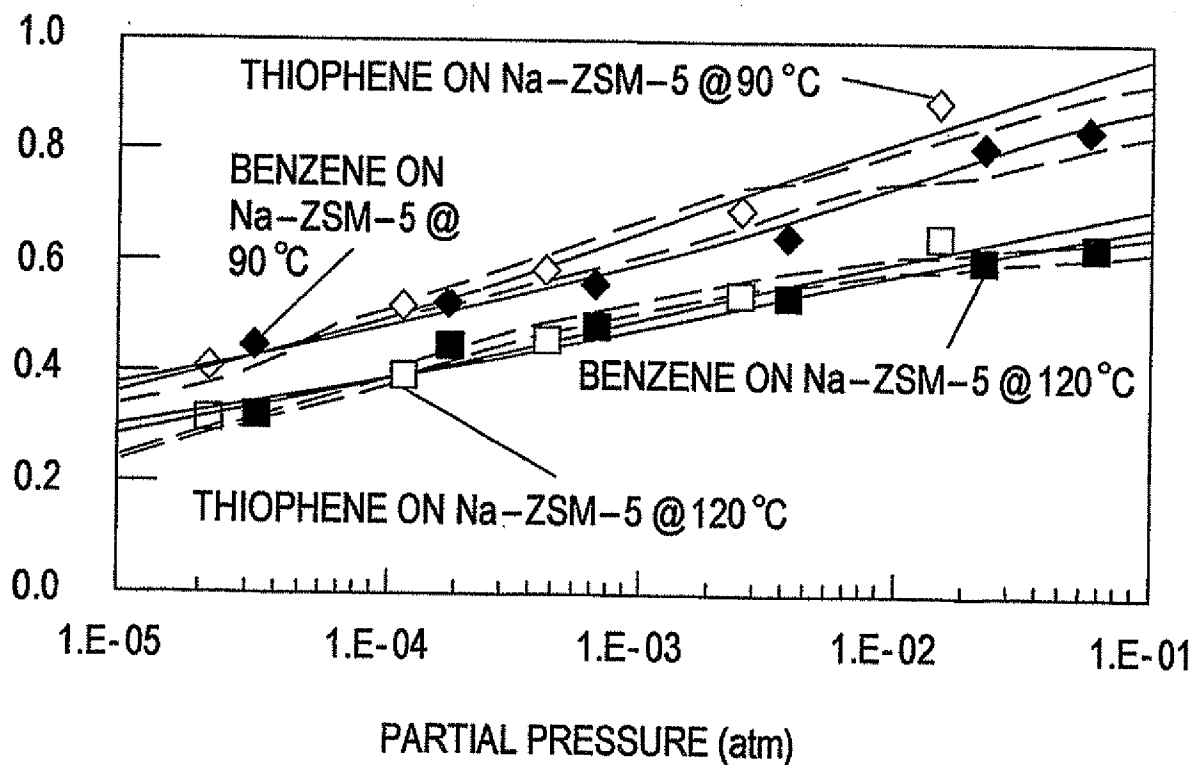


FIG 10

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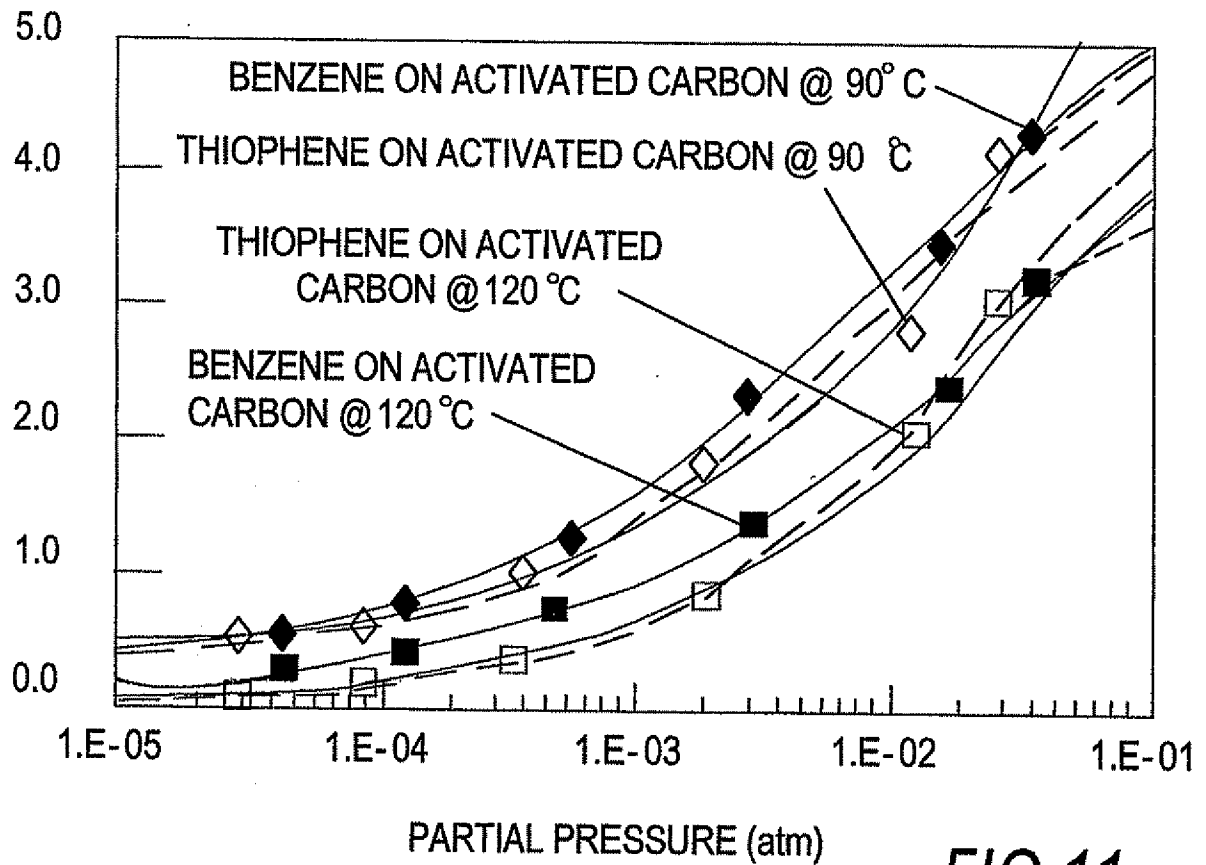


FIG 11

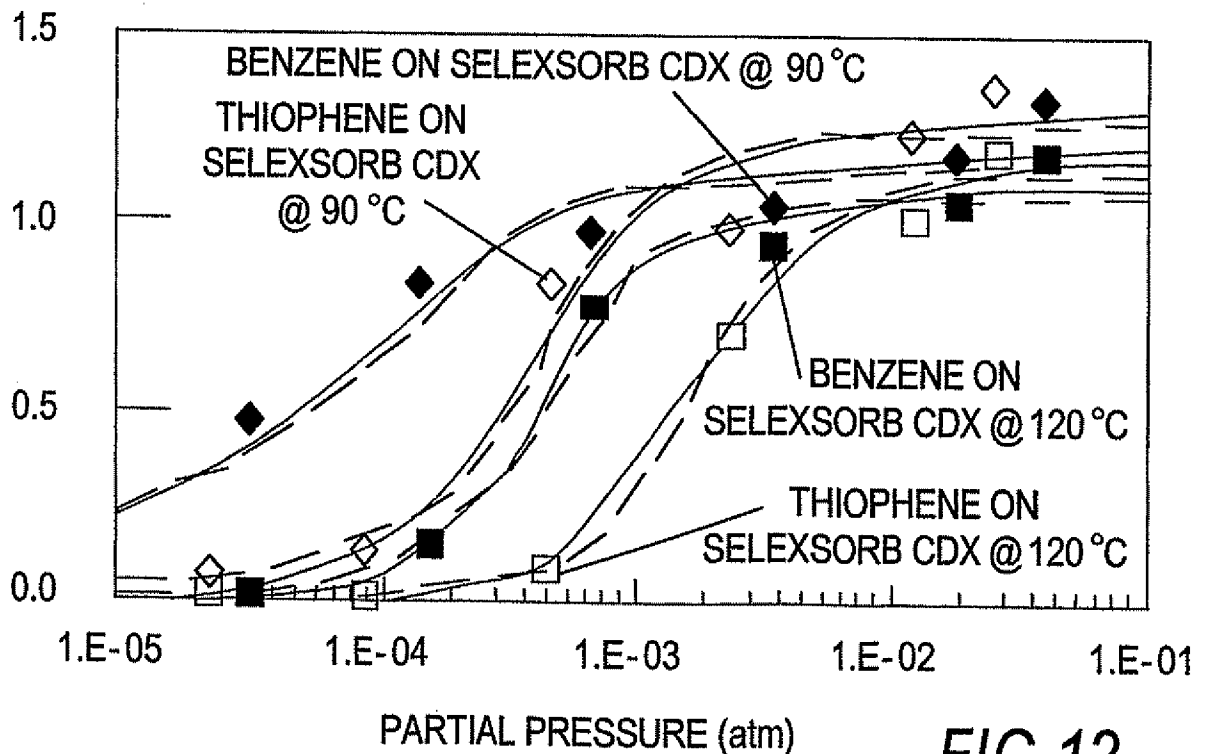


FIG 12

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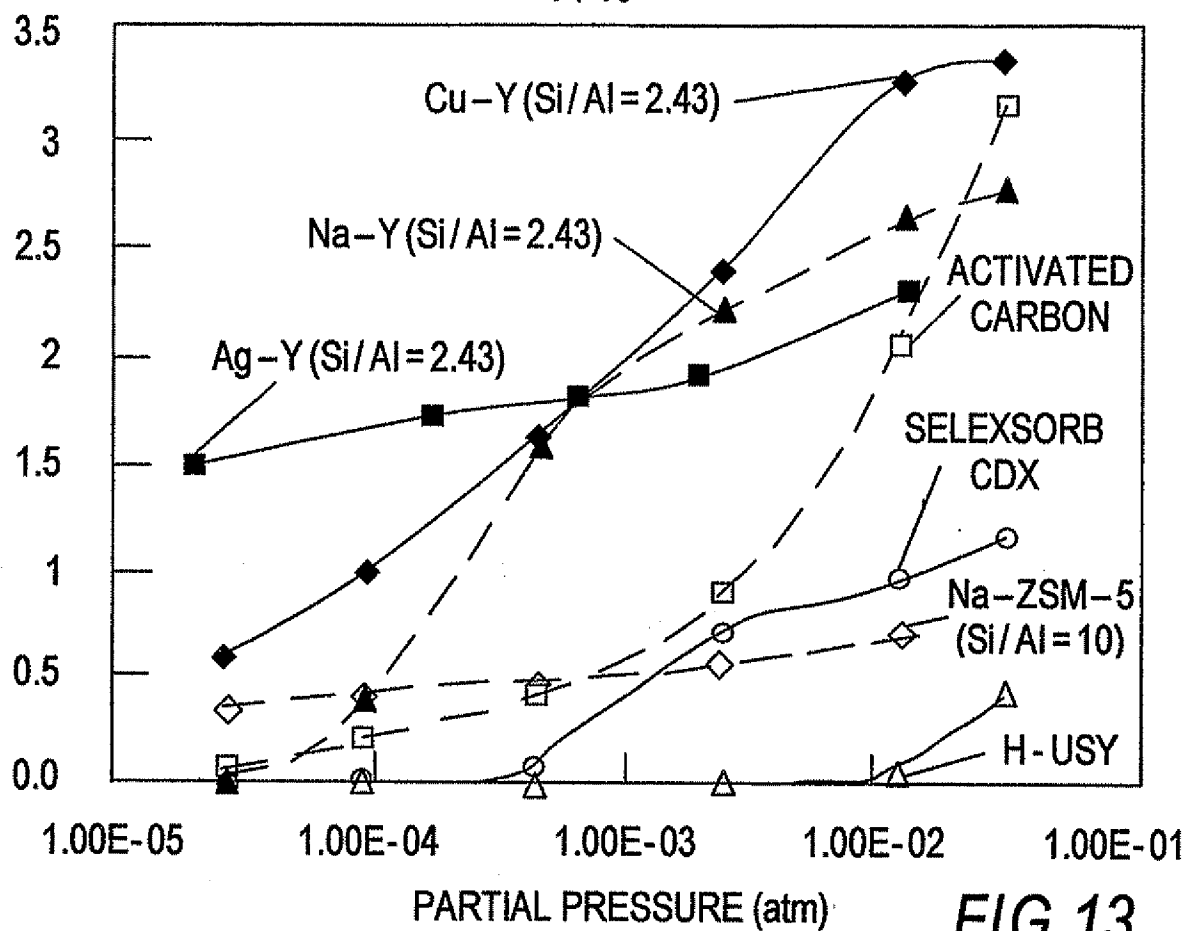


FIG 13

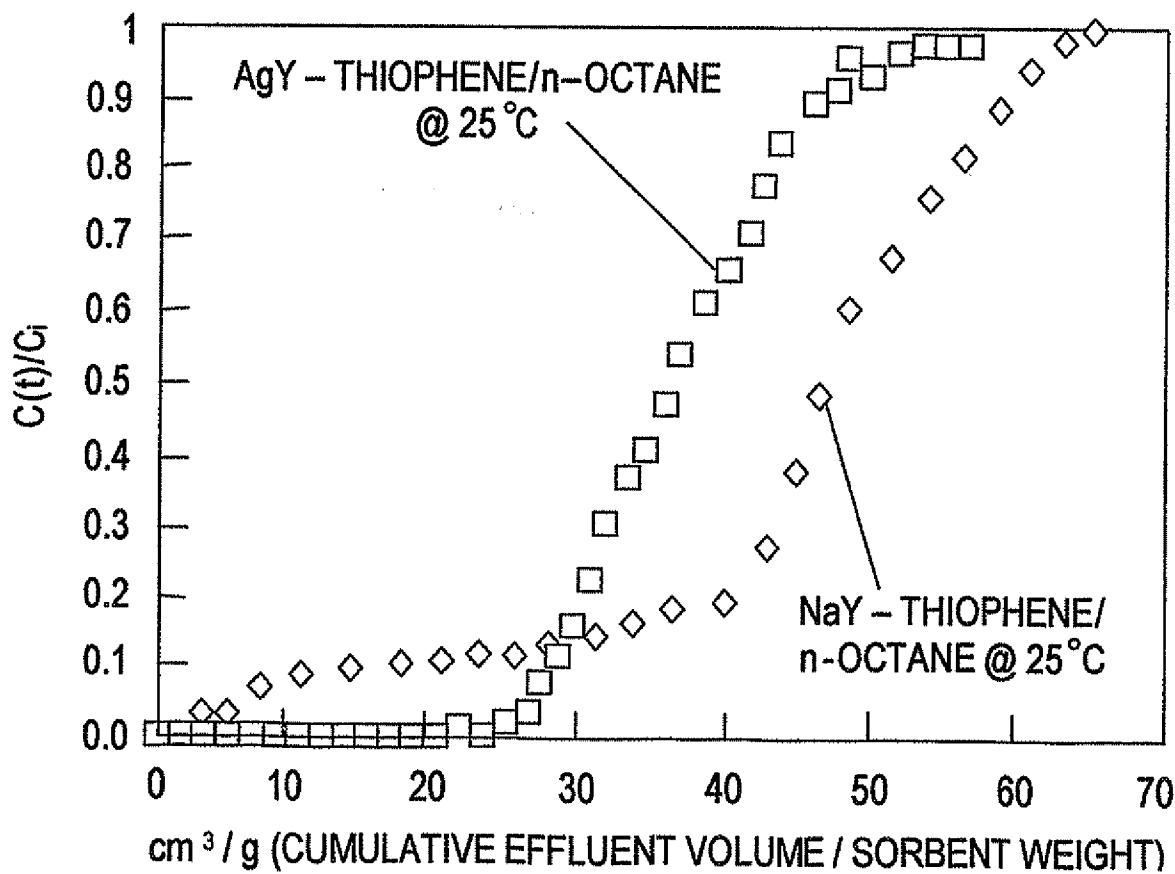
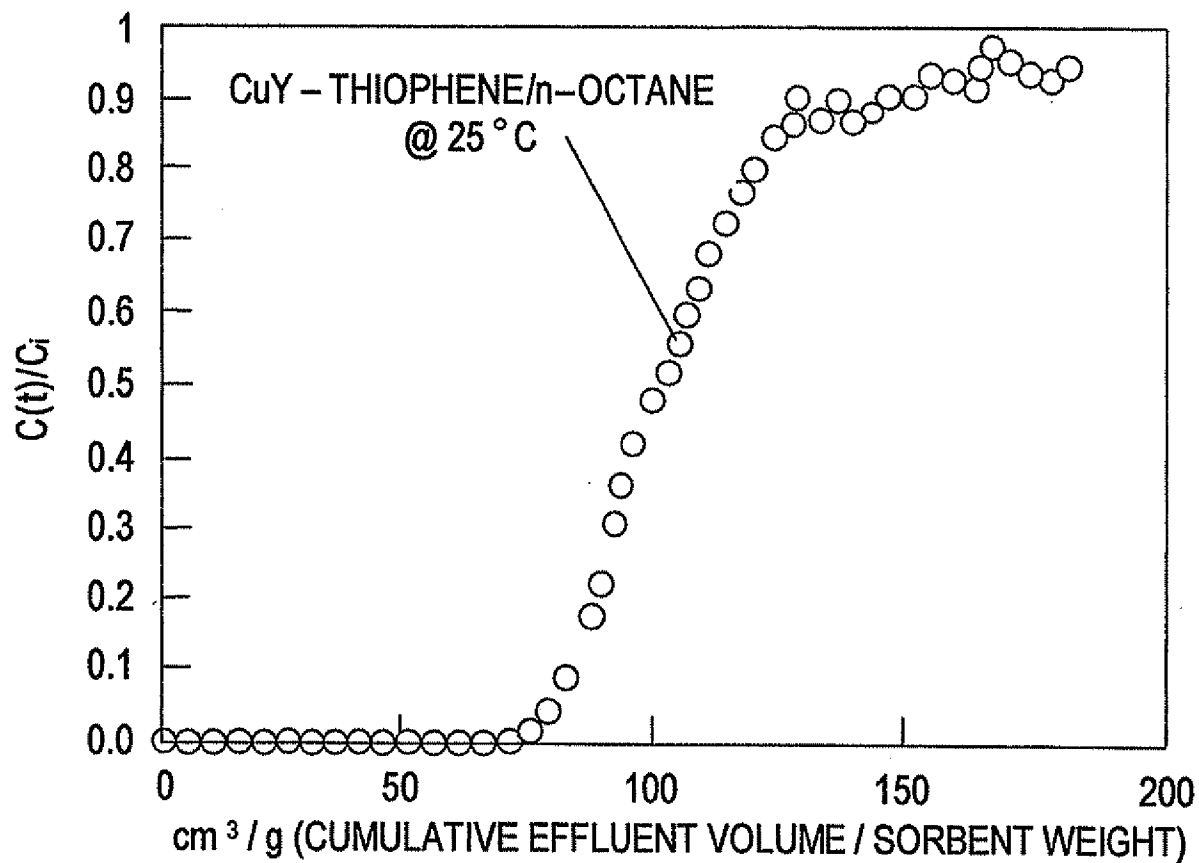
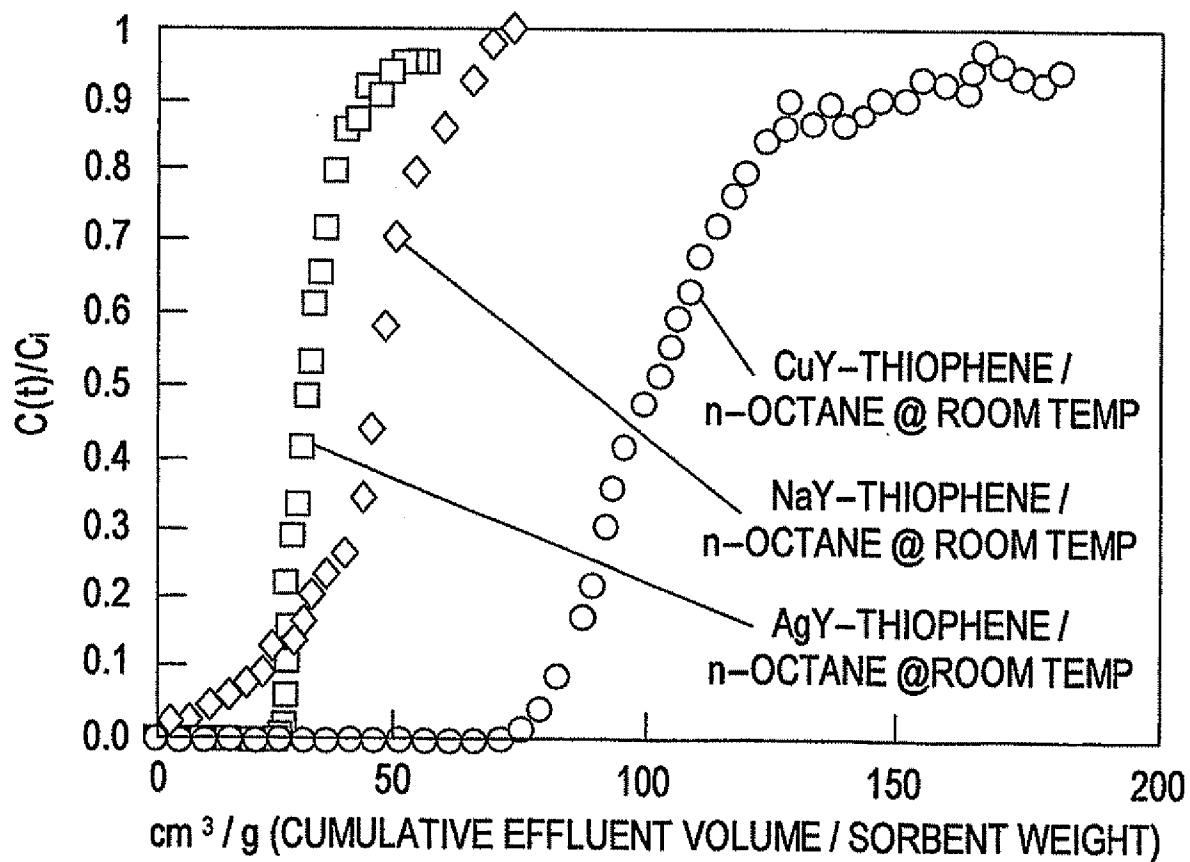


FIG 14

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**FIG 15****FIG 16**

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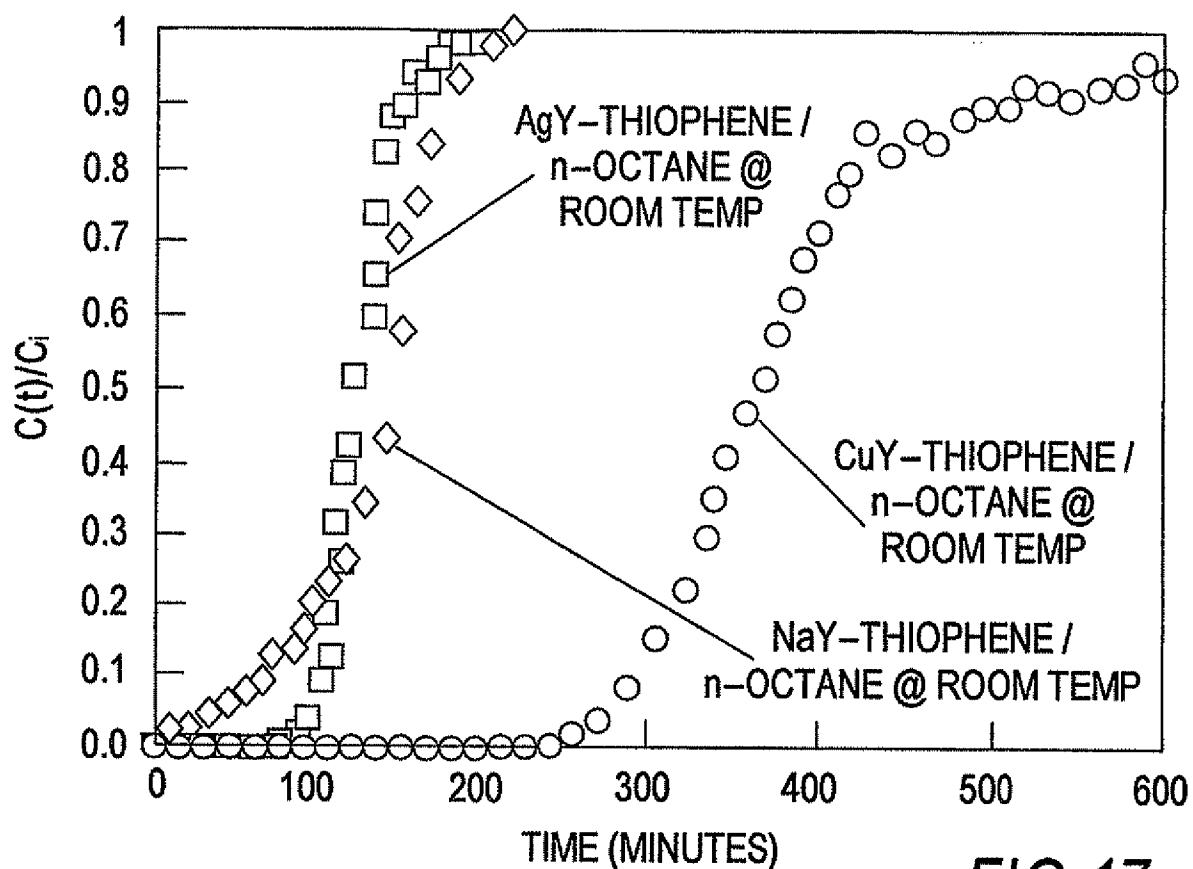


FIG 17

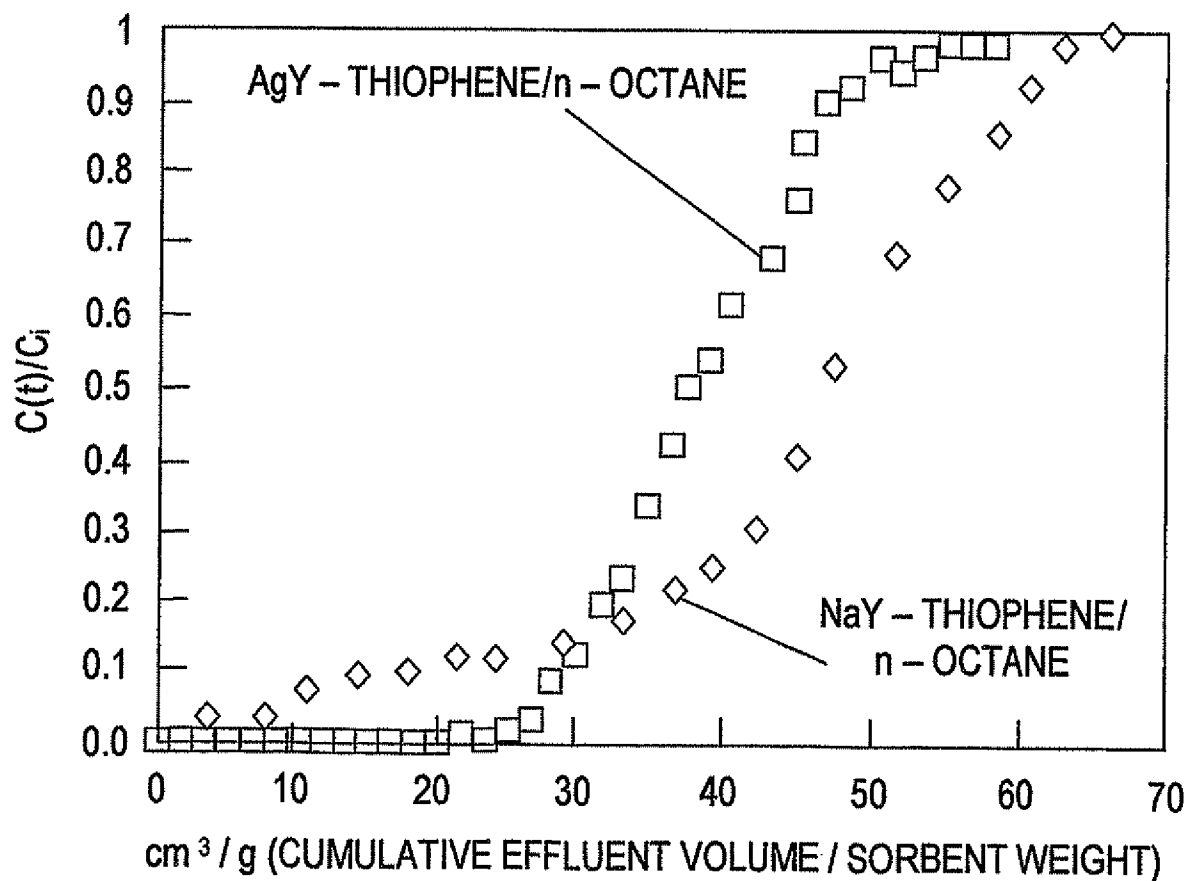
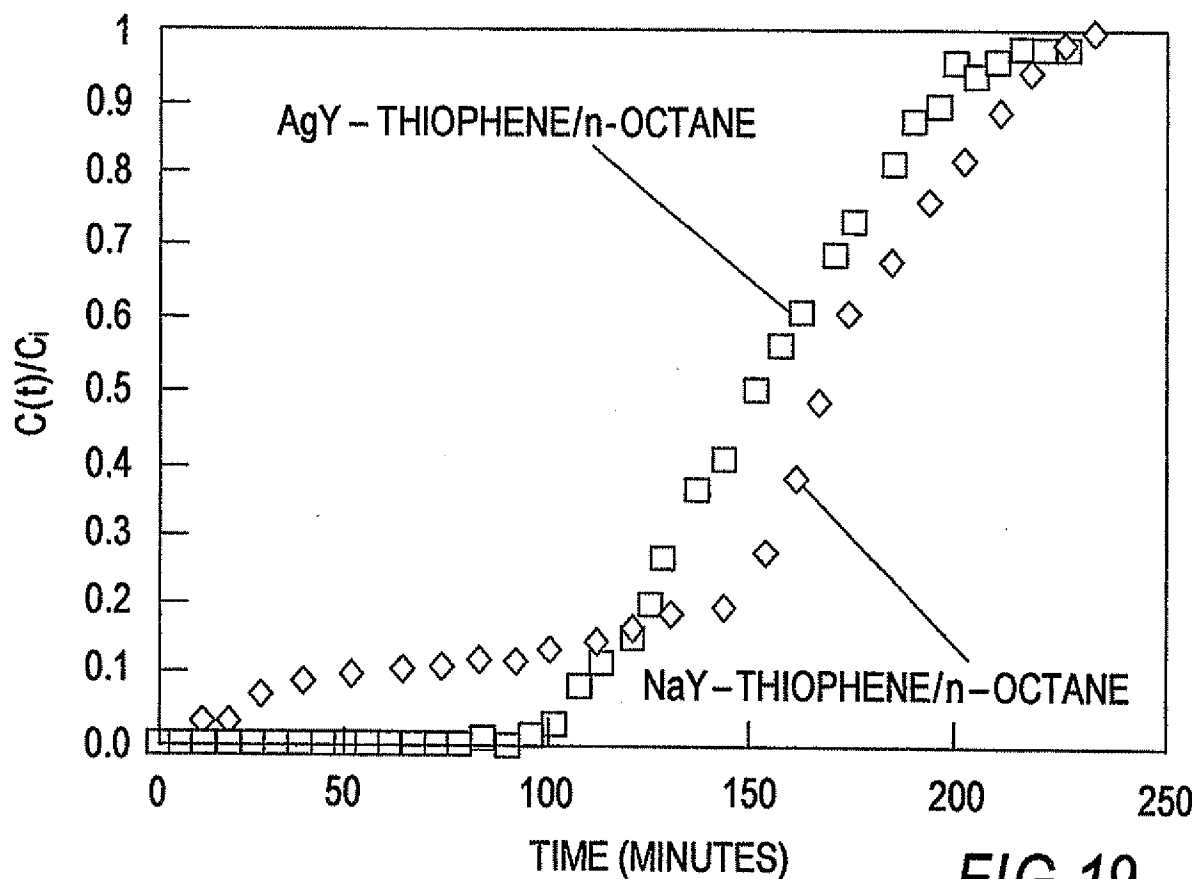
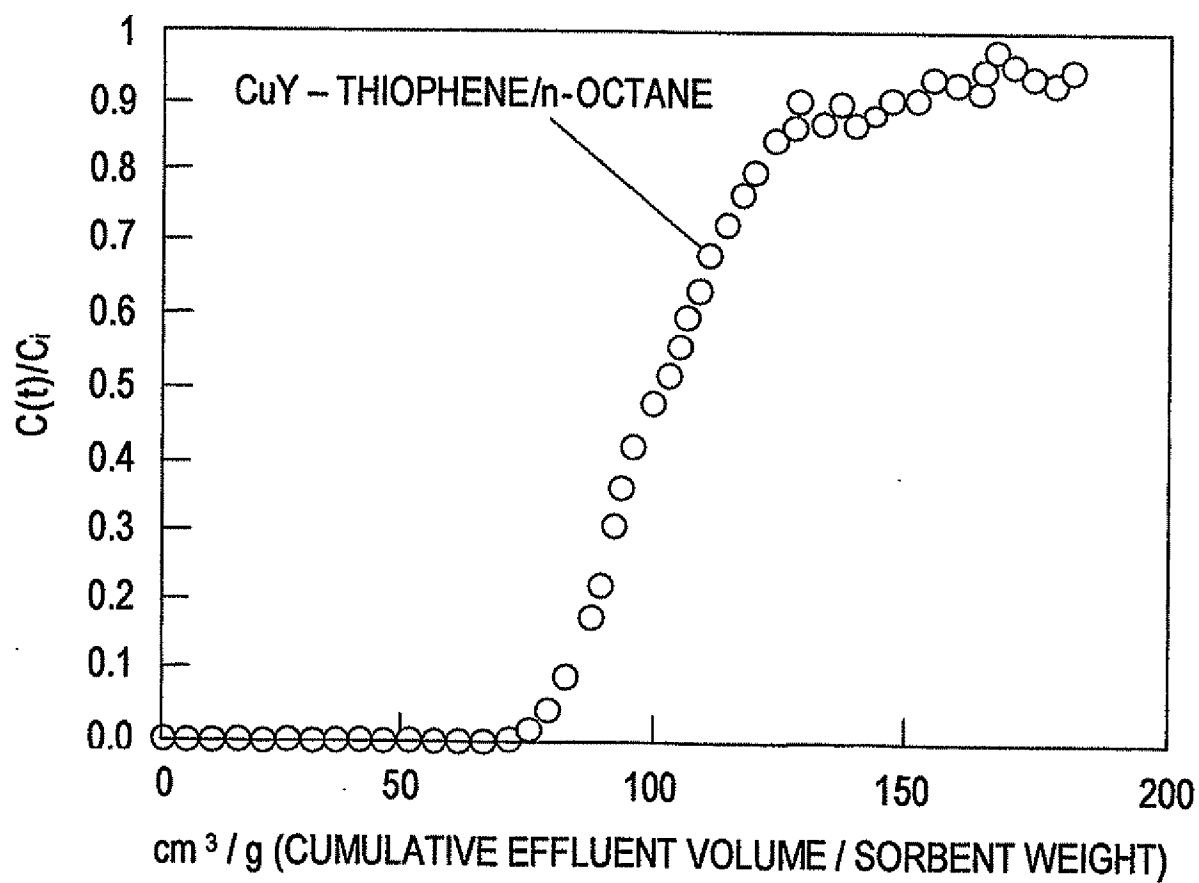


FIG 18

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**FIG 19****FIG 20**

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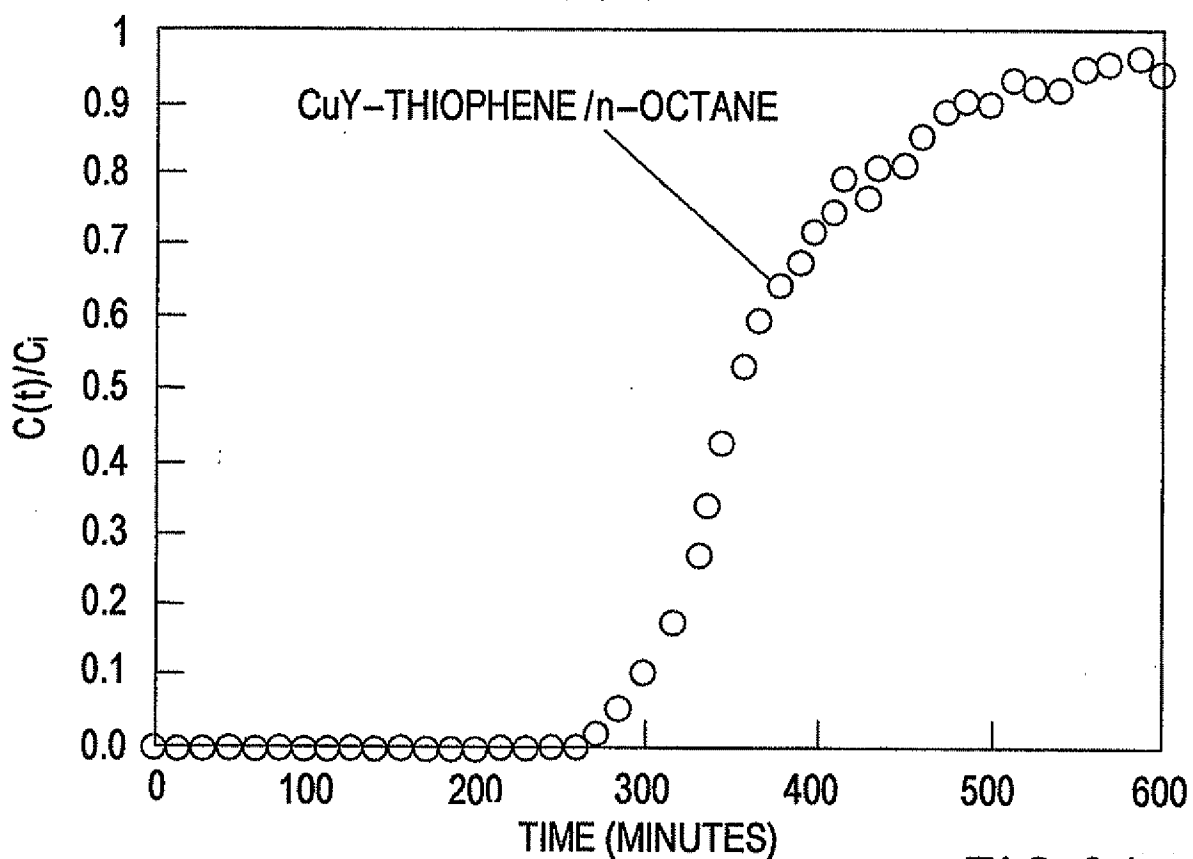


FIG 21

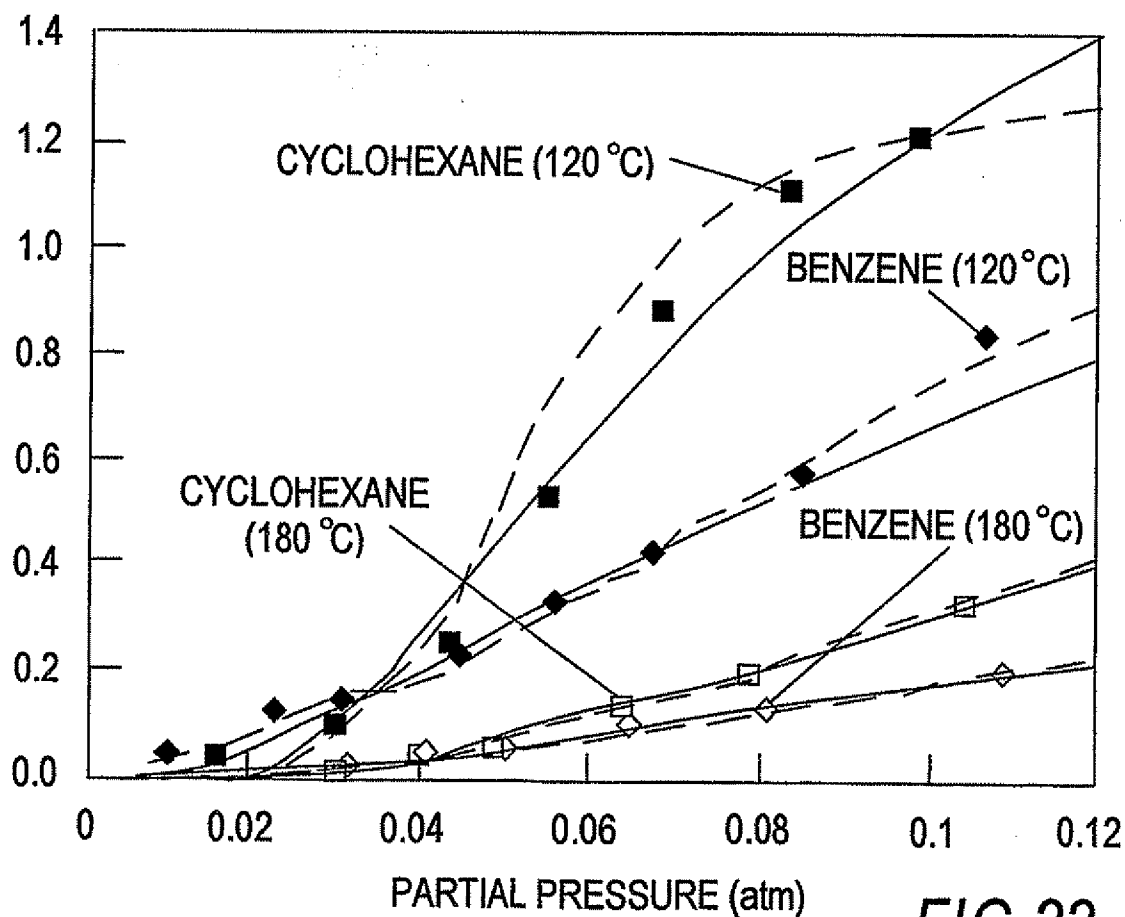


FIG 22

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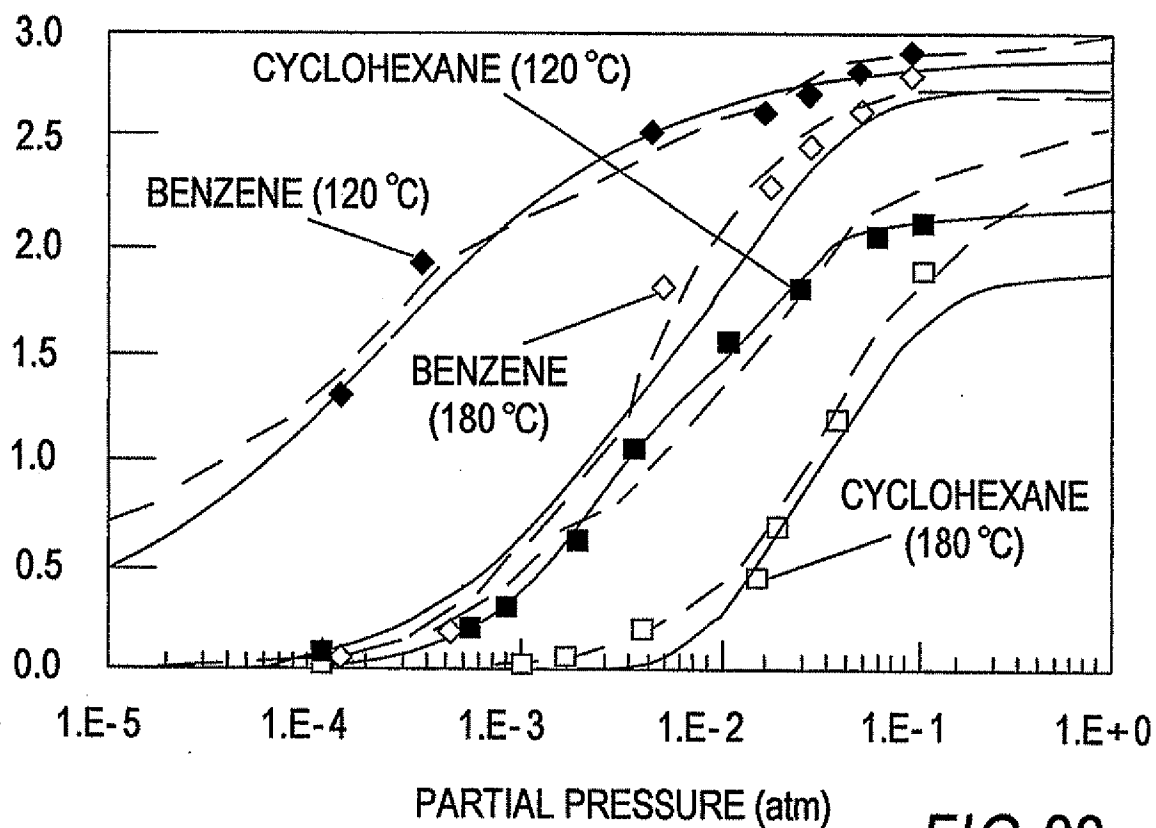


FIG 23

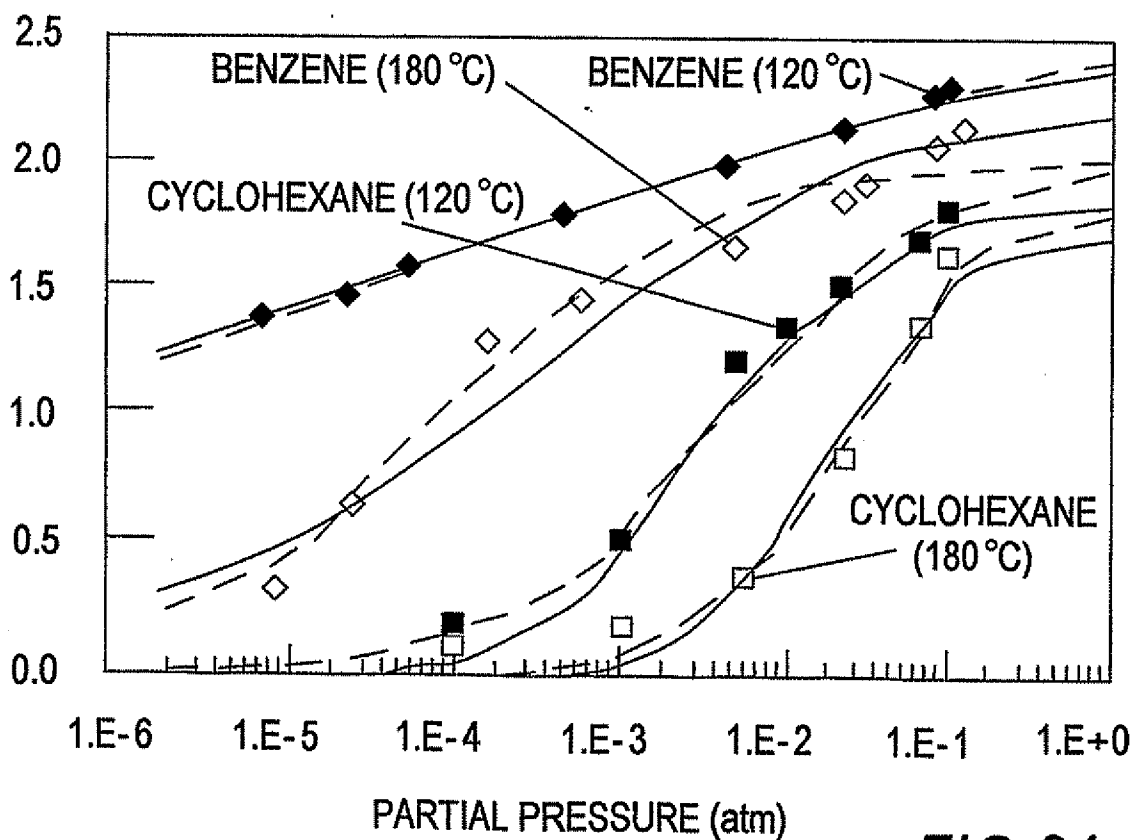


FIG 24



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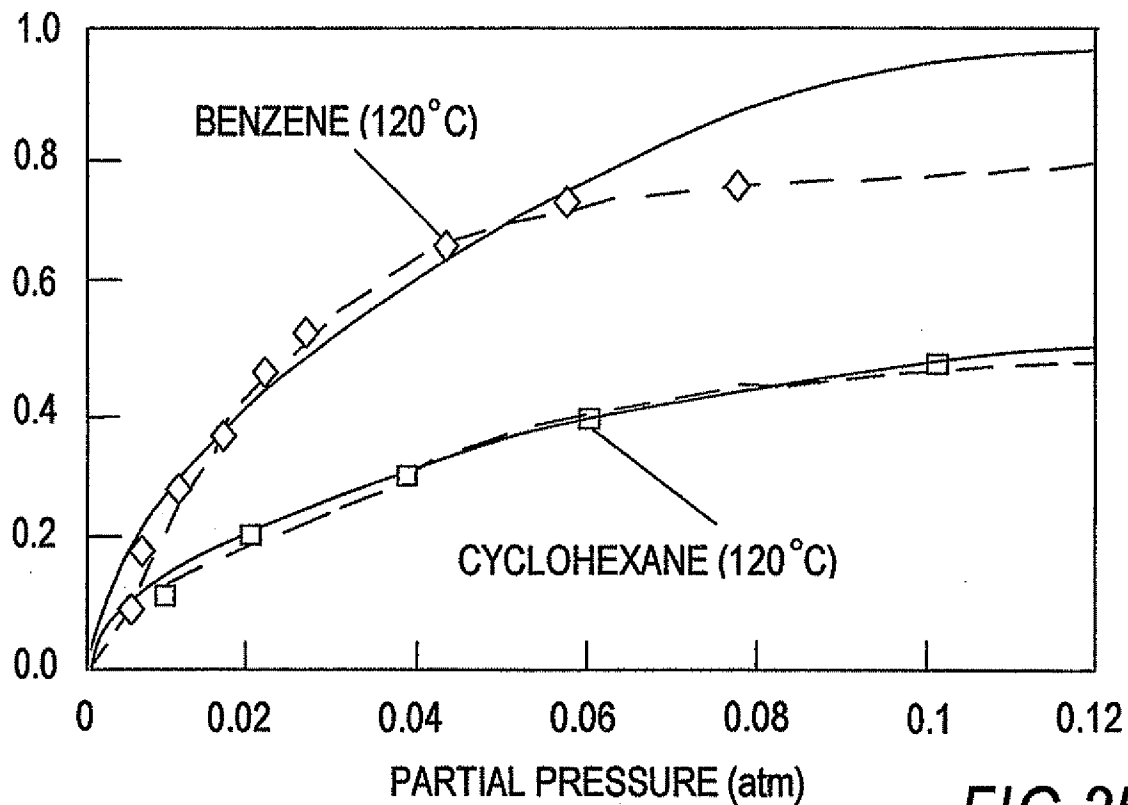


FIG 25

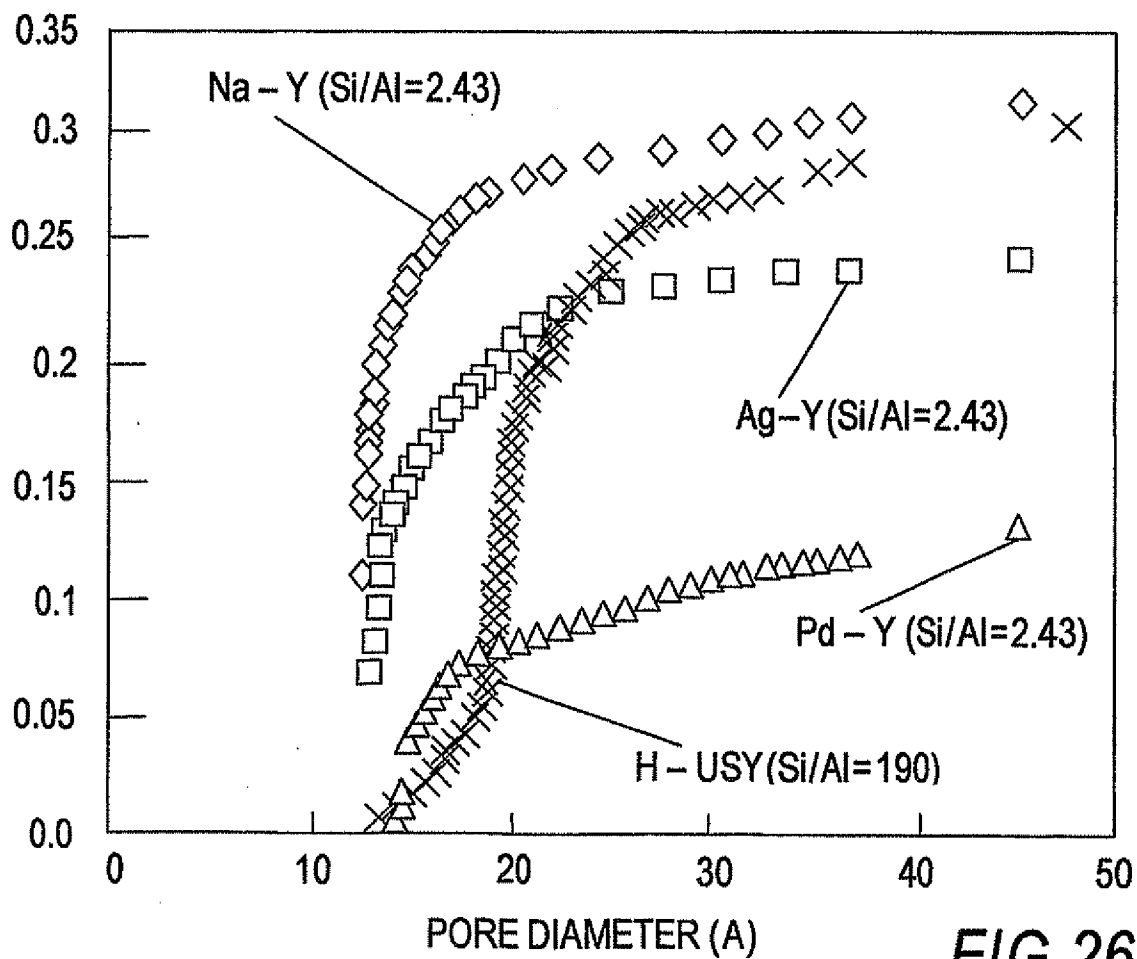


FIG 26

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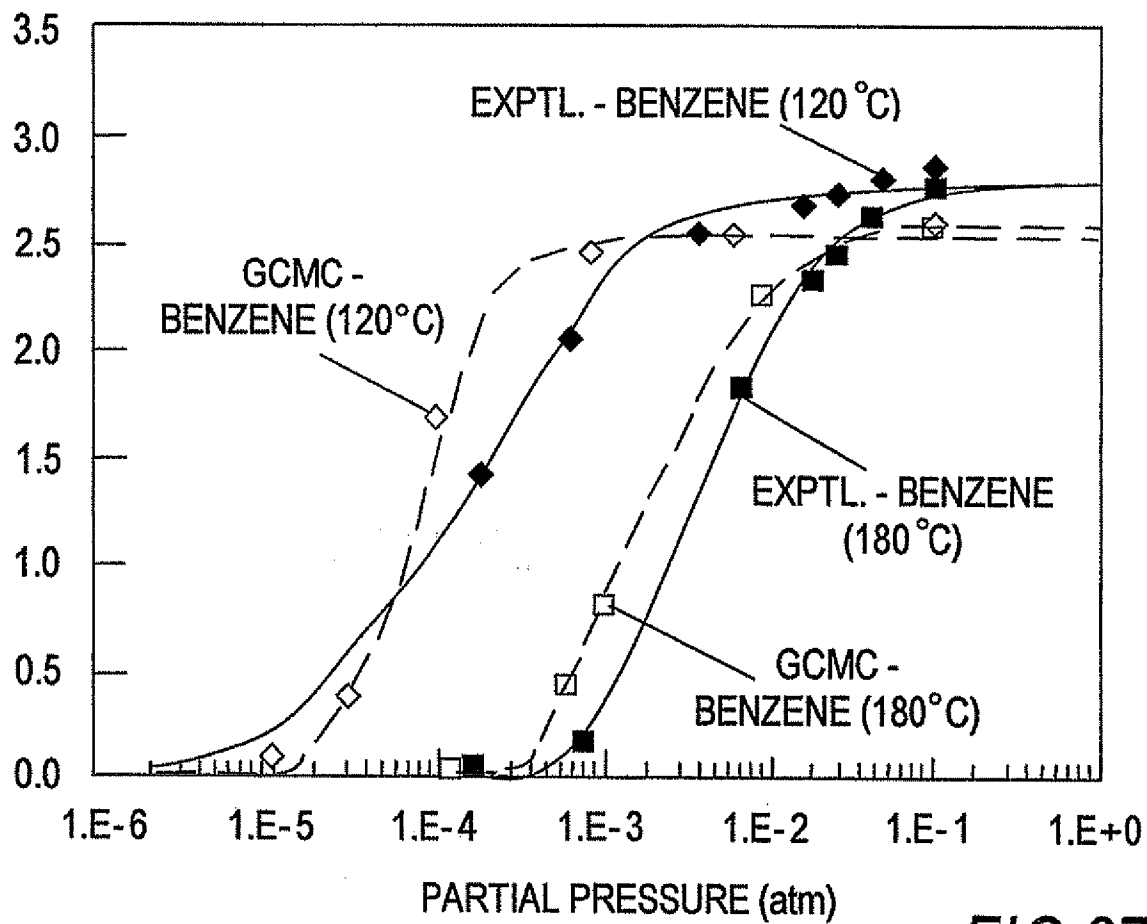


FIG 27

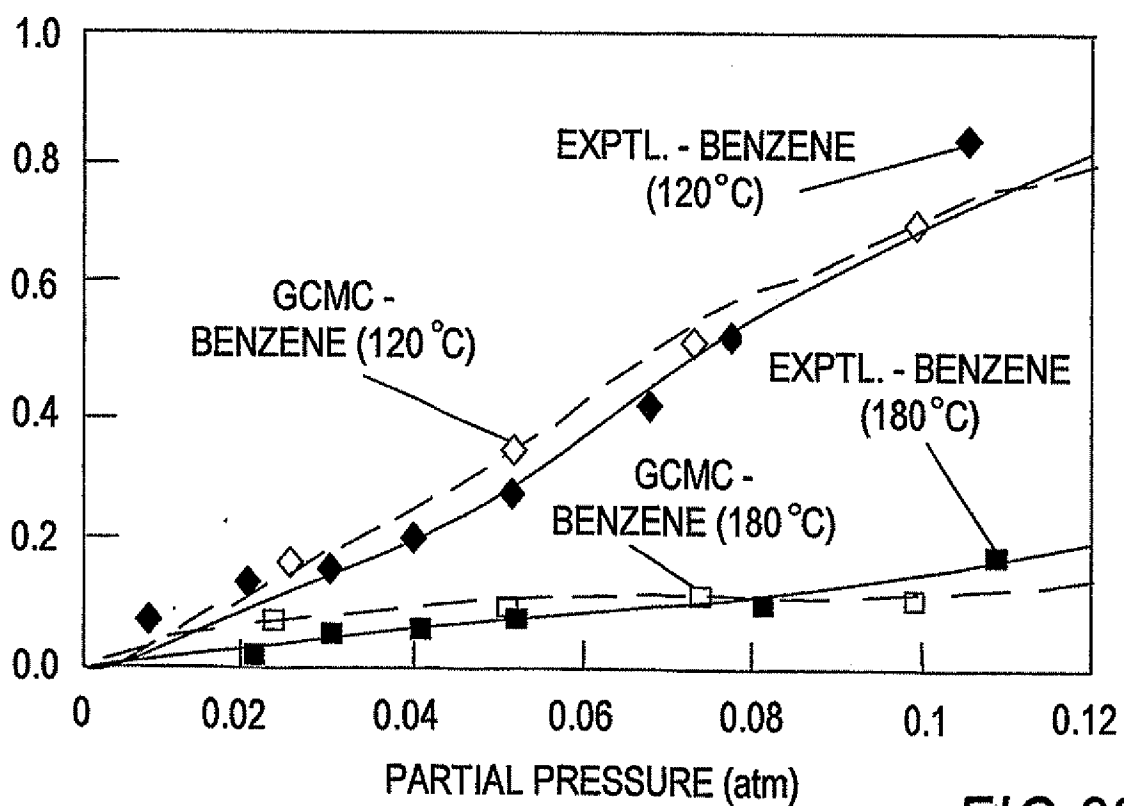


FIG 28

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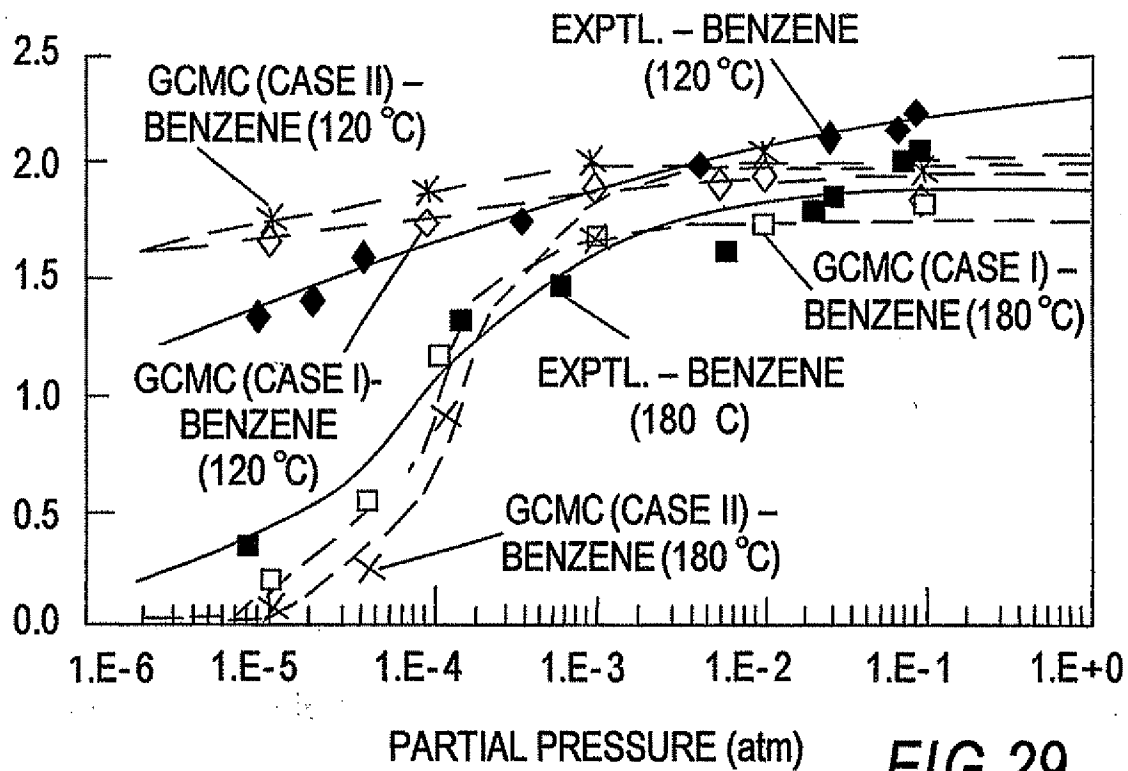


FIG 29

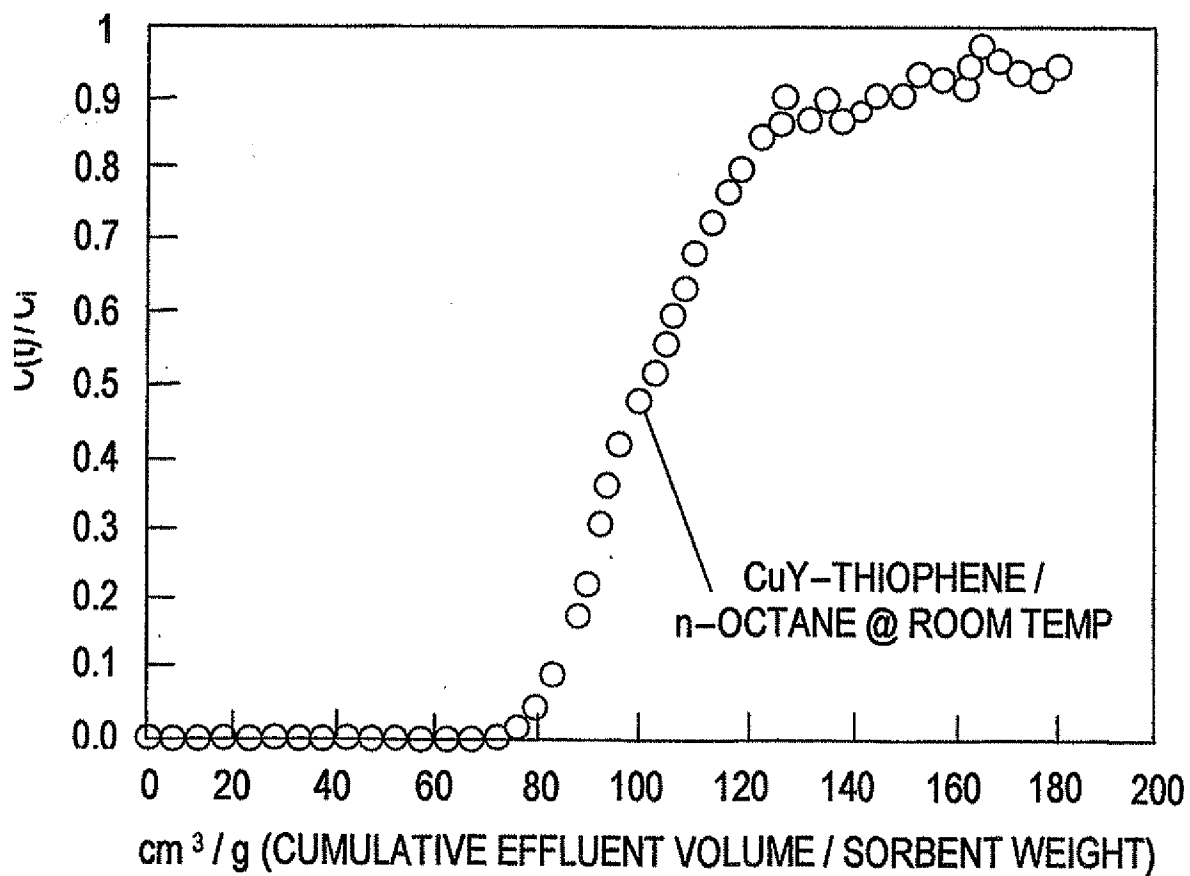


FIG 30

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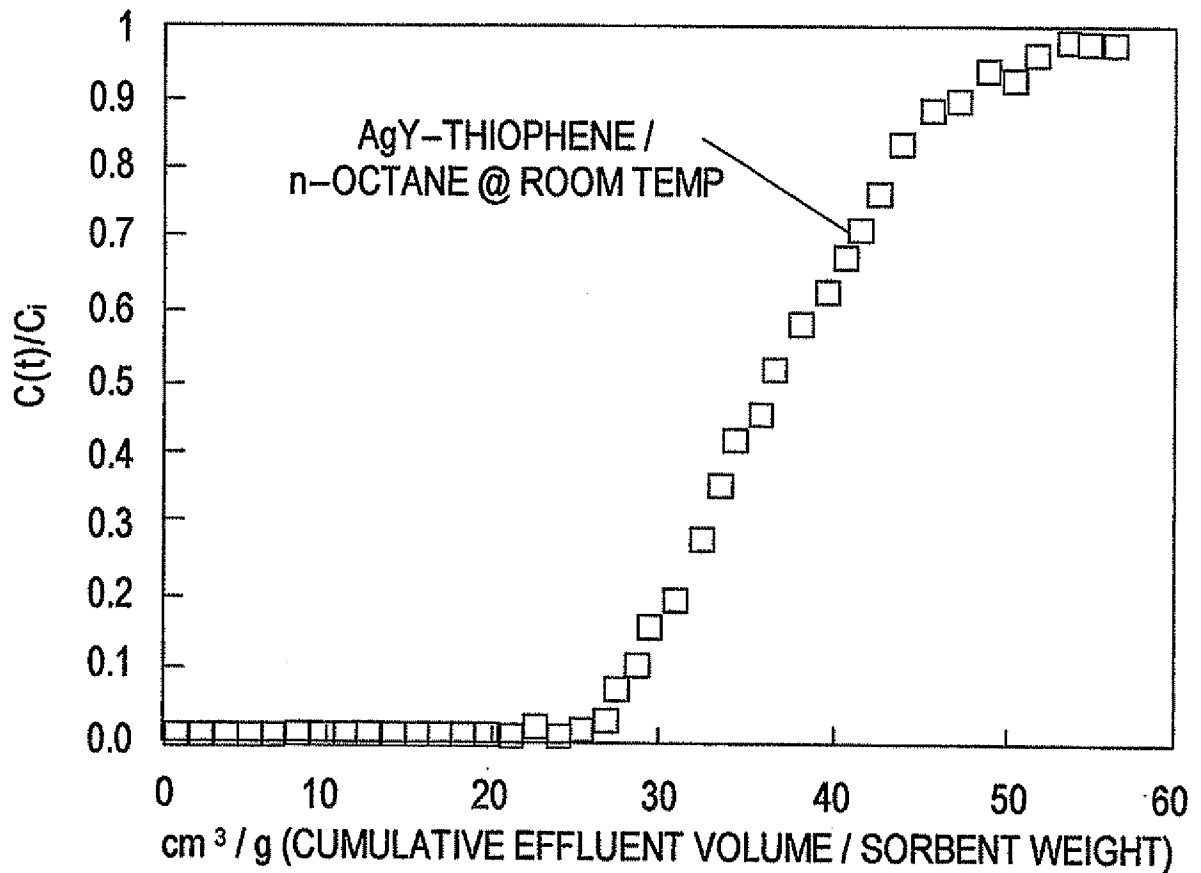


FIG 31

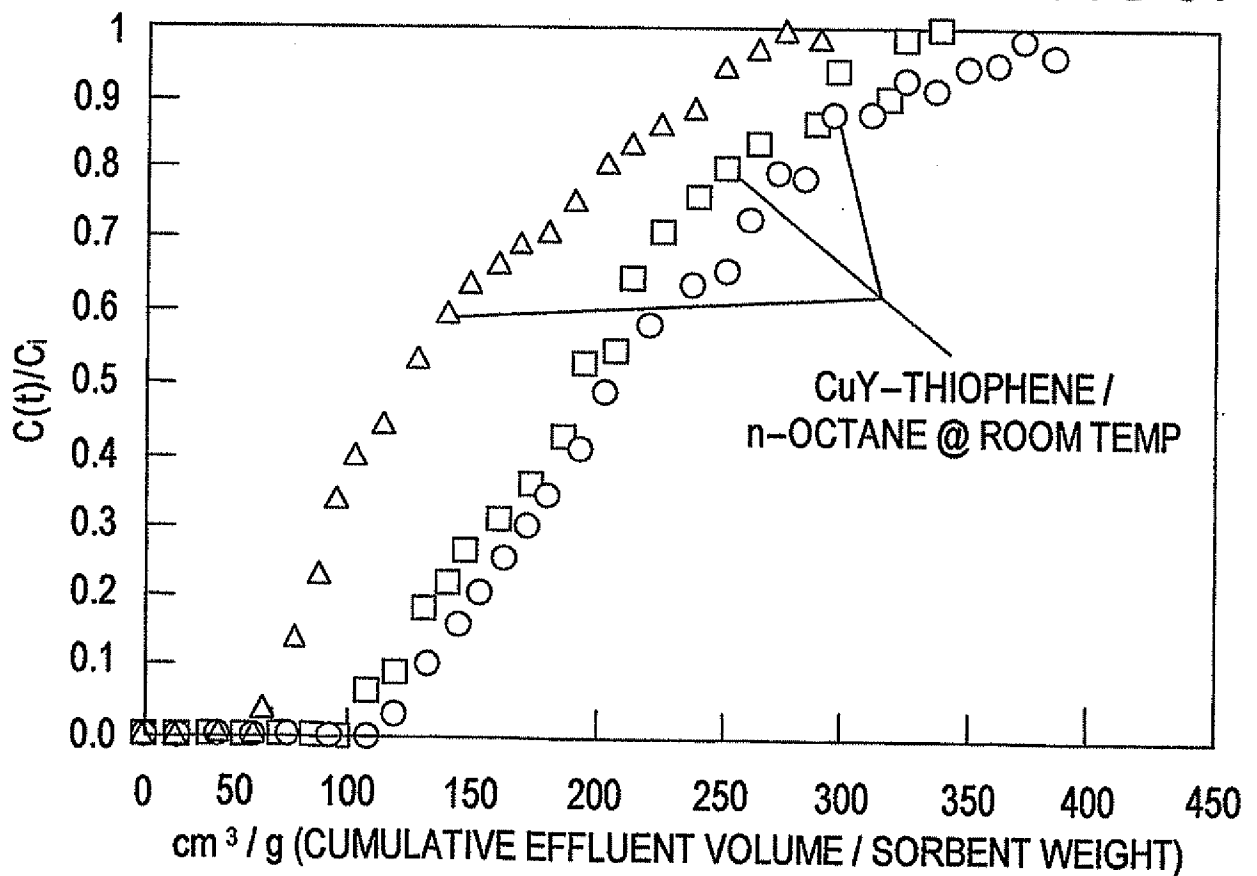


FIG 32



(19) World Intellectual Property Organization  
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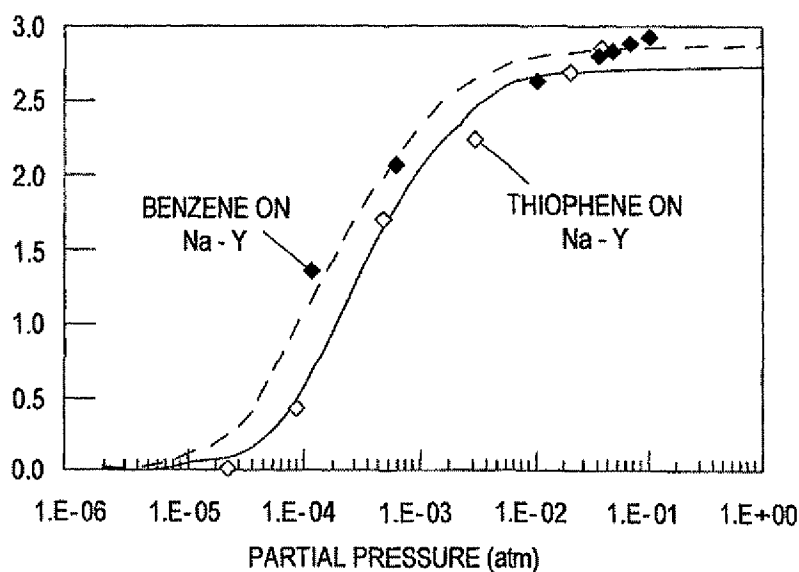
(74) Agent: **DIERKER, Julia, Church**; Dierker & Glassmeyer, P.C., 3331 W. Big Beaver Road, Suite 109, Troy, MI 48084-2813 (US).

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[Continued on next page]

(54) Title: SELECTIVE SORBENTS FOR PURIFICATION OF HYDROCARBONS



(57) Abstract: Cu Y and Ag Y zeolites as selective sorbents for desulfurization of liquid fuels. Thiophene and benzene were used as the model system, and vapor phase isotherms were measured. Compared with NaY, CuY and AgY adsorbed significantly larger amounts of both thiophene and benzene at low pressures. It is hypothesized that this is due to  $\pi$ -complexation with  $\text{Cu}^+$  and  $\text{Ag}^+$ . On a per-cation basis, more thiophene was adsorbed by  $\text{Cu}^+$  than by  $\text{Ag}^+$ , eg. 0.92 molecule/ $\text{Cu}^+$  versus 0.42 molecule/ $\text{Ag}^+$  at  $2 \times 10^{-5}$  atm and 120 °C. Molecular orbital calculations confirmed the relative strengths of  $\pi$ -complexation: thiophene > benzene and  $\text{Cu}^+$  >  $\text{Ag}^+$ . The experimental heats of adsorption for  $\pi$ -complexation are in qualitative agreement with theoretical predictions. The invention further comprises a process and sorbents for removal of aromatics from hydrocarbons.



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— with international search report

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6 November 2003

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

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PCT/US 02/28040

According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C106

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, API Data, CHEM ABS Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| X          | US 4 188 285 A (MICHLMAYR MANFRED J)<br>12 February 1980 (1980-02-12)<br>cited in the application<br>the whole document<br>--- | 1,3                   |
| X          | EP 0 275 855 A (SOPAR SA NV)<br>27 July 1988 (1988-07-27)<br>cited in the application<br>claim 1; examples<br>---<br>-/--      | 1,3                   |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

28 April 2003

Date of mailing of the international search report

16. 05. 03

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Authorized officer

Keipert, 0



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/28040

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X          | <p>DATABASE CA 'Online!<br/> CHEMICAL ABSTRACTS SERVICE, COLUMBUS,<br/> OHIO, US;<br/> LUO, GUOHUA ET AL: "Removal of thiophene<br/> from coke-oven benzene by selective<br/> adsorption on zeolites"<br/> retrieved from STN<br/> Database accession no. 132:110289<br/> XP002228841<br/> abstract<br/> &amp; RANLIAO HUAXUE XUEBAO (1999), 27(5),<br/> 476-480,</p> | 1,3                   |
| X          | <p>US 6 118 037 A (SANFILIPPO DOMENICO ET<br/> AL) 12 September 2000 (2000-09-12)<br/> claim 1; examples 1-13; tables I,II</p>  | 2,4                   |
| Y          | <p>WO 98 56875 A (SANSON EMMANUELLE ;VRINAT<br/> MICHEL (FR); LAMURE VALERIE (FR); LEMAIR)<br/> 17 December 1998 (1998-12-17)<br/> claims 1,3,14,22</p>   | 1-4                   |
| Y          | <p>US 6 215 037 B1 (MUNSON CURTIS L ET AL)<br/> 10 April 2001 (2001-04-10)<br/> cited in the application<br/> claim 1</p>   | 1-5                   |
| A          | <p>DE 39 40 428 A (RUETGERSWERKE AG)<br/> 13 June 1991 (1991-06-13)<br/> claims 1-6</p>   | 1-4                   |
| A          | <p>US 4 179 361 A (MICHLMAYR MANFRED J)<br/> 18 December 1979 (1979-12-18)<br/> examples 1,3</p>  | 1-4                   |
| Y          | <p>PATENT ABSTRACTS OF JAPAN<br/> vol. 003, no. 068 (C-048),<br/> 13 June 1979 (1979-06-13)<br/> &amp; JP 54 041844 A (TORAY IND INC),<br/> 3 April 1979 (1979-04-03)<br/> abstract</p>   | 5                     |
| Y          | <p>PATENT ABSTRACTS OF JAPAN<br/> vol. 004, no. 151 (C-028),<br/> 23 October 1980 (1980-10-23)<br/> &amp; JP 55 098123 A (TORAY IND INC),<br/> 25 July 1980 (1980-07-25)<br/> abstract</p>  | 5                     |
|            | <p>---</p> <p>-/--</p>  |                       |

## INTERNATIONAL SEARCH REPORT

 International Application No.  
 PCT/US 02/28040

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| X          | TAKAHASHI, AKIRA ET AL:<br>"Aromatics/aliphatics separation by<br>adsorption: new sorbents for selective<br>aromatics adsorption by pi.-complexation"<br>INDUSTRIAL & ENGINEERING CHEMISTRY<br>RESEARCH,<br>vol. 39, no. 10,<br>14 September 2000 (2000-09-14), pages<br>3856-3867, XP002238899<br>cited in the application | 6                     |
| Y          | abstract<br>page 3856, left-hand column -page 3857,<br>left-hand column<br>page 3860 -page 3861   | 5                     |
| X          | GB 2 005 299 A (SHELL INT RESEARCH)<br>19 April 1979 (1979-04-19)<br>page 1, line 32 -page 2, line 3  | 6                     |
| A,P        | US 6 423 881 B1 (PADIN JOEL ET AL)<br>23 July 2002 (2002-07-23)<br>column 6, line 10 - line 46  | 6                     |
| A          | DD 208 628 B (LEUNA WERKE VEB)<br>4 April 1984 (1984-04-04)<br>the whole document   | 6                     |
| A          | US 3 960 703 A (DIELACHER MAXIMILIAN ET<br>AL) 1 June 1976 (1976-06-01)<br>claims   | 6                     |
| A          | XIE Y.-C. ET AL.: "Spontaneous Monolayer<br>Dispersion of Oxides and Salts onto<br>Surfaces of Supports: Applications to<br>Heterogeneous Catalysis"<br>ADVANCES IN CATALYSIS,<br>vol. 37, 1990, pages 1-43, XP009009745<br>the whole document  | 2,4,6                 |

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 02/28040

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.